Fluidized Bed Coal Desulfurization

Final Report

Maddury Ravindram

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ABSTRACT

Preliminary studies on Fluidized Bed Coal Desulfurization were conducted at the Jet Propulsion Laboratory, California Institute of Technology, under the NRC-NASA Associateships Program and JPL Director's Discretionary Fund for the period December 14, 1981, through December 14, 1982.

Laboratory scale experiments were conducted on two high-volatile bituminous coals in a bench scale batch fluidized bed reactor. Chemical pre-treatment and post-treatment of coals were tried as a means of enhancing desulfurization. Sequential chlorination and dechlorination-cum-hydrodesulfurization under modest conditions relative to the water-slurry process were found to result in substantial sulfur reductions of about 80%. Sulfur forms as well as proximate and ultimate analyses of the processed coals are included.

These studies indicate that a fluidized bed reactor process has considerable potential for being developed into a simple and economic process for coal desulfurization.

PREFACE

ACKNOWLEDGMENTS

FOREWORD

This report is based on the experimental results of Fluidized Bed Coal
Desulfurization studies conducted at the Jet Propulsion Laboratory under a DDF
grant during the period December 14, 1981, through December 14, 1982. The
study covers chlorination, dechlorination and hydrodesulfurization of two high
volatile bituminous coals in a laboratory-scale batch fluidized bed reactor.
A follow-on program is planned that addresses itself to parametric estimation
and detailed kinetics studies on coal desulfurization in a fluidized bed
reactor.

CONTENTS

I. INTRODUCTION

The Jet Propulsion Laboratory (JPL) initiated development of the Chlorinolysis Process for Coal Desulfurization in 1976 under the JPL Director's Discretionary Fund. The preliminary results of coal desulfurization by chlorinolysis attracted Bureau of Mines funding for a four-month laboratory screening study of 12 bituminous, subbituminous and lignite coals obtained from the Eastern, Midwestern and Western regions of the United States (Ref. 1). The follow-on work in Phases II and III (Ref. 2 and 3) was funded by the United States Department of Energy (DoE) and included substantial modification and development of the process to provide process improvements and reduced process costs.

Following Phase II and Phase III, a subsequent DoE-funded study titled "Coal Desulfurization by Chlorinolysis-Production and Combustion Test Evaluation of Product Coals" (Ref. 4) was conducted to determine the ignition and burning characteristics of these coals at the Pennsylvania State "plane flame furnace." These combustion test evaluations represent a "first" to any of the chemical coal cleaning processes.

The current Fluidized Bed Coal Desulfurization Program was conducted under the JPL Director's Discretionary Fund. Two coals, PSOC 276 (Pittsburgh coal from Harrison County, Ohio) and PSOC 282 (Illinois No. 6 coal from Jefferson County, Illinois) were chosen for the study. The study included several chlorination, dechlorination and hydrodesulfurization tests in a laboratory scale fluidized bed reactor. Some of the product coals as well as raw and chlorinated coals were subjected to washing treatments. This report includes the results of the laboratory fluidized bed reactor tests, the influence of process parameters and product evaluation by LECO analyses for total sulfur in the laboratory, and more complete analyses carried out by the Colorado School of Mines Research Institute (CSMRI), which were conducted from December 14, 1981 through December 14, 1982.

II. SUMMARY

This is the final report for the Fluidized Bed Coal Desulfurization studies conducted at the Jet Propulsion Laboratory, California Institute of Technology at Pasadena, California, under a JPL Director's Discretionary Fund (DDF) grant for the period December 14, 1981, through December 14, 1982.

The scope of the work consisted of several phases: (1) design and fabrication of a laboratory-scale fluidized bed reactor system for coal desulfurization; (2) laboratory-scale tests consisting of sequential chlorination, dechlorination and/or hydrodesulfurization on two high-volatile bituminous coals; and (3) assessment of the influence of pre-treatments to raw coals and chlorinated coals, and post-treatment of processed coals on the extent of sulfur removed.

Laboratory-scale screening tests with PSOC 276 and PSOC 282 coals were used to investigate: (1) the feasibility of coal desulfurization in the solid state, (2) the effect of reaction time and temperature on chlorination, (3) the effect of employing a mixture of nitrogen and chlorine during chlorination, (4) the effect of reaction time and temperature during hydrodesulfurization and dechlorination, (5) the influence of an alkaline wash to raw coal, chlorinated coals and hydrodesulfurized coals, and (6) the specific advantages of coal desulfurization in a gas fluidized bed reactor as compared to the chlorinolysis process employing coal-water slurries.

Results of the studies indicate that: (1) the two coals studied could be desulfurized to approximately the same levels achieved in the chlorinolysis process by reacting dry coal in a sequential manner with chlorine, nitrogen and/or hydrogen. Up to 80% sulfur reductions could be achieved in considerably reduced times of reaction as compared to the chlorinolysis process. (2) Prolonged chlorination or chlorination at higher temperatures did not result in any enhanced desulfurization over chlorination for 15 min at 100°C. In fact, chlorination for even 5 min resulted in substantial sulfur reduction. The exothermicity of coal-chlorine reaction made it possible to maintain the reactor at about 100°C without any external source of heating. (3) Employing a mixture of nitrogen and chlorine in the ratio of 4:1 during chlorination results in significant sulfur removal in the process. Consequently, considerably lower chlorine concentrations could be employed. (4) Hydrodesulfurization of chlorinated coals at 700°C for 30 min was more efficient in removing the sulfur from coal as compared to simple dechlorination employing nitrogen. Hydrodesulfurization for as short a period as 10 min results in significant sulfur reductions. (5) Pretreatment of raw and chlorinated coals, as well as processed coals with 1 M Na_2CO_3 solution for 30 min substantially reduces sulfur emissions in combustion as indicated by LECO analysis for total sulfur. (6) Coal desulfurization in the solid state in a gas fluidized bed reactor has a tremendous potential over the chlorinolysis process employing coal-water slurries such as reduced reaction times, lower chlorine requirement, lower cost of processing and a simple process with fewer processing steps.

III. CONCLUSIONS AND RECOMMENDATIONS

1. Preliminary experimental results on coal desulfurization in a fluidized bed reactor have demonstrated the potential of the process in providing a simple and cost effective method of converting high sulfur coals to environmentally acceptable solid fuels for the power plants and utility boilers.

2. The results indicate that coal desulfurization achieved in the fluidized bed process is comparable to that achieved in a coal-water slurry system.

3. Chlorination times as low as five minutes were found to result in desulfurization levels of about 60%. This represents a substantial reduction in the chlorination time as compared to the slurry process and hence the reactor cost.

4. Because dry coal is used as the feed to the fluidized bed reactor, the coal sulfur leaves as gaseous species from the chlorination reactor, which is likely to result in reduced chlorine requirement in the process. This was also evident from the fact that a mixture of nitrogen and chlorine in the proportion of 4:1 during chlorination did not significantly reduce the extent of coal desulfurization. Because chlorine cost represents a substantial portion of the overall process cost, the reduced chlorine requirement will have a significant effect on the process economics.

5. Dechlorination and hydrodesulfurization of the chlorinated coal has been demonstrated in 10 minutes in the fluidized bed reactor which represents a substantial reduction over the time required in the slurry process.

6. A fluidized bed reactor provides good mixing of the coal particles and contact between the gas-solid phase, thereby facilitating better process control and isothermal operation.

7. Thermal efficiency of the overall process will be high because all the reaction steps are brought about in the solid phase itself.

8. The reduction in processing steps and improved process control should result in enhanced product yields and lower costs.

9. While the feasibility of bringing about coal desulfurization in a fluidized bed has been clearly demonstrated, extensive development is required to establish the optimum range of operating conditions.

10. Further fundamental work is required on fluidized bed coal desulfurization to understand the basic chemistry and kinetics of the reactions involved in the process.

3

IV. COAL DESULFURIZATION

The ever increasing demand for energy, uncertainties associated with resources of petroleum and natural gas, inherent problems with nuclear power plants and current unfavourable economics of solar energy and biomass utilization have been primary contributory factors for the renaissance of coal as a sustainable energy resource for the next decade and beyond. However, utilization of coal for power generation and process heat is beset with environmental problems. The major problem with coal combustion units is that associated with sulfur dioxide emissions although emissions of nitrogen oxides, particulates and trace elements also contribute to environmental degradation. In the last decade, several alternatives for controlling sulfur dioxide emissions from coal combustion units have been proposed. These can be broadly classified as:

(1) Use of low sulfur content coals.

(2) Pre-combustion physical and chemical coal cleaning.

(3) Retention of sulfur in the ash during combustion.

(4) Post-combustion flue-gas cleanup.

Reserves of coal that contain sufficiently low concentrations of sulfur to enable them to meet the present emission standard of 1.2 lb $SO_2/10^6$ Btu (which corresponds to 0.7 wt% sulfur in coal with a heating value of 12,000 Btu/lb) are both limited and restricted to specific geographical locations. In fact, only 12.3% of U.S. coal reserves are within this compliance level. The major recoverable fractions of Eastern and Midwestern U.S. coals contain more than 2 wt% sulfur.

Precombustion physical coal cleaning to remove mineral matter is widely practiced in the coal industry. By the conventional float-sink methods as much as 60% of the pyritic sulfur in coal is also removed. However, a significant portion of coal is also rejected along with the high density material of high sulfur content. In addition, physical methods are not effective in removing organic sulfur content of coal, which in certain cases may constitute 50% of the sulfur in coal. Thus to decrease the sulfur content in coal to acceptable levels, it is necessary to remove both pyritic and organic sulfur fractions by chemical methods. During the last decade several chemical coal cleaning methods have been proposed. However, a majority of these methods are applicable for the removal of only pyritic sulfur, and no chemical coal desulfurization process uniformly applicable for the removal of both inorganic and organic sulfur fractions in coal is as yet available commercially.

Retention of sulfur during combustion employing dolomite, limestone, etc., in fluidized bed combustion units is studied widely. Chemical modification of coal and incorporation of alkaline earth metals into the coal matrix as a means of retaining sulfur in the ash have also been proposed.

Among the post-combustion gas-cleaning methods, the most widely adopted one is flue gas desulfurization (FGD) employing wet scrubbers. However, scrubbers generate large quantities of sludge, which must be disposed of economically. Also, in many instances scrubbers are unreliable, requiring excessive maintenance. Consequently, the cost of a FGD facility represents a substantial proportion of the equipment cost of a coal-fired power plant, and this proportion was found to increase as the size of the plant decreases, thereby making FGD prohibitively expensive for small utility boilers. Dry scrubbers overcome some of the problems associated with wet scrubbers.

The economical production of coals that comply with environmental regulations for SO_2 emissions remains the main incentive for the development of chemical coal cleaning processes. However, many of the chemical treatment methods remove only up to 40% of the organic sulfur, which limits their application. In addition, while the New Source Performance Standards (NSPS) of 1.2 lb $SO_2/10^6$ Btu could be met by most of the chemical coal cleaning methods, a majority of these methods may not be effective in meeting the revised NSPS of 1979, which stipulates 90% reduction in potential SO_2 emissions. However, recent research effort in chemical coal cleaning has resulted in the development of processes capable of removing sulfur levels exceeding 90 wt%. DOE is currently evaluating three processes as prime candidates for coal desulfurization: JPL's Low-Temperature Chlorinolysis process, TRW's Gravimelt process and General Electric's Microwave process. However, commercialization of chemical coal cleaning technology may be delayed by economic factors.
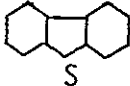
JPL initiated work on coal beneficiation and coal desulfurization a few years ago. An outgrowth of this activity is the JPL Low-Temperature Chlorinolysis Process for coal desulfurization. The initial laboratory studies indicated that the process was capable of removing up to 70% total sulfur from an Illinois No. 6 bituminous coal. Since then the process has been considerably modified. A recent process modification involves aqueous phase chlorination, followed by solid phase dechlorination and/or hydrodesulfurization, which is capable of removing up to 90% of the total amount of sulfur.

V. SULFUR IN COAL

Sulfur in coal exists primarily in two forms, inorganic and organic, in almost equal proportions. The average sulfur content in coals varies from 0.5 to 7%, depending on the source and location of the deposit.

The major constituent of inorganic sulfur is iron sulfide, FeS_2, commonly known as pyrite although it may occur in different crystalline states such as pyrite (cubic) and marcasite (orthorhombic). The other forms of inorganic sulfur in coal are sulfate sulfur and elemental sulfur, which are normally present in very low concentrations. Sulfate sulfur occurs mainly as gypsum and iron sulfate, the latter resulting from the oxidation of pyrites during storage and exposure. The low concentration of sulfate sulfur, together with its solubility in water, makes it of little consequence during coal cleaning. The concentration of elemental sulfur in coal is also very small. Pyrite in general is believed to be present as a discrete phase in coal, which incidentally facilitates its removal by float-sink methods. However, with very fine particles even complete pyritic sulfur removal is not possible.

Organic sulfur in coal is thought to be uniformly distributed and firmly bound to the coal matrix. Limited information exists on the specific organic sulfur compounds and their distribution in various coals. It is generally accepted that a major proportion of organic sulfur in coal is made up of the following functional groups:

(1) Aliphatic or aromatic   R-SH
    Thiols (Mercaptans, Thiophenols)   Ar-SH

(2) Aliphatic or aromatic sulfides   R-S-R
    and mixtures of these (Thioethers)   Ar-S-Ar
                                       R-S-Ar

(3) Aliphatic or aromatic disulfides   R-S-S-R
    and mixtures of these (Bisthioethers) Ar-S-S-Ar
                                       R-S-S-Ar

(4) Heterocyclic compounds of the
    thiophenic type (Dibenzothiophene)

Analysis of coals for organic sulfur fractions has shown that lignite and high-volatile bituminous coals contain relatively higher concentration of thiols and also that higher ranked coals have a higher proportion of thiophenic sulfur. More extensive classification and characterization of coals, particularly for organic sulfur components and their quantitative distribution, are needed. In general, there is a lack of understanding of the chemical reactions involving organic sulfur in the different chemical coal cleaning processes, which is partly due to the nonavailability of analytical techniques for the direct determination of organic sulfur. Recent studies on desulfurization of model organic sulfur compounds of the type

6

believed to be present in coal by some of the proposed processes have shown that many of these compounds are unreactive and that more fundamental research work is needed to understand the nature of the precise organic sulfur species in coal and their reactivities under different desulfurization conditions.

VI. CHEMICAL COAL CLEANING METHODS

Among the various methods that have been proposed for controlling the SO_2 emissions from coal fired power plants, precombustion coal desulfurization offers several potential advantages over flue gas desulfurization. In the past decade several processes have been proposed for extracting pyritic and organic sulfur from coal. There are also as many processes that are modifications of a process or a combination of different processes. However, most of these could be classified into a few groups based on the chemistry of the reactions involved in the process:

    (1) oxidation reactions.

    (2) displacement reactions.

    (3) reduction reactions.

A further classification is also possible, depending on whether the reactions are brought about in the liquid phase or in the solid phase. However, very few studies of the latter type are reported. In general, in the liquid phase methods, the sulfur in coal is transformed into a soluble form.

The exposure of coal to air results in a slow oxidation of pyrite to the sulfate, which is water soluble. A majority of the processes reported for the removal of pyritic sulfur in coal are aimed at enhancing this natural process of oxidation. Oxidatants ranging from metal ions (Fe^{3+}) to strong acids (HNO_3), oxygen, air, SO_2, Cl_2, H_2O_2, NO_2, etc. have been employed for this purpose. The PTEC oxydesulfurization process, AMES wet oxidation process, LEDGEMONT oxygen leaching process, ARCO-promoted oxydesulfurization process, TRW Meyers desulfurization process, and JPL chlorinolysis process, among others, all involve oxidizing the sulfur fraction in coal to sulfuric acid or to a soluble sulfate. There is a wide variability in processing conditions and in the removal efficiencies among the various processes. The JPL Low Temperature Chlorinolysis process is, however, one of the few processes capable of removing both inorganic and organic sulfur from coal.

Processes based on the displacement of sulfur, such as the Battelle Hydrothermal process, TRW Gravimelt process, and the General Electric Microwave process involve heating coal with sodium hydroxide to remove the sulfur in the form of sulfides and polysulfides. The TRW Gravimelt process, in addition to removing sulfur, also removes substantial quantities of mineral matter from coal. However, one major disadvantage of using caustic is that the excess sodium retained in coal may cause severe ash slagging problems in the boiler.

Among the processes based on reduction, mention may be made of the IGT flash desulfurization process for producing chars. The process involves preliminary air oxidation of coal to facilitate sulfur removal in the subsequent hydrodesulfurization step. A sulfur acceptor such as calcium oxide or iron oxide was found to limit the hydrogen consumption during the latter step.

Many of the chemical coal cleaning processes described above were found to be effective for the almost total removal of pyritic sulfur and partial removal of organic sulfur. On the basis of total sulfur removals claimed, most of these processes are capable of desulfurizing a large number of coals to meet the 1971 U.S. NSPS for SO_2 emissions (1.2 lb/10^6 Btu) while only a few may be able to satisfy the revised 1979 standard, which stipulates 90% reduction in potential SO_2 emissions to the atmosphere, irrespective of the initial sulfur content of coal. There also exists some uncertainty regarding the extent of organic sulfur removal achieved in these processes primarily because of the lack of precise analytical methods for the direct determination of organic sulfur in coal. In practice, the actual reduction in organic sulfur may be much lower than claimed. Consequently, there is a need for a better understanding of the sulfur forms in coal and a more realistic appraisal of the cost and efficiency of the chemical coal cleaning processes.

A. COAL DESULFURIZATION BY CHLORINE

Chlorination of coal was initially studied for producing non-caking coals and chlorohydrocarbons. Coal desulfurization by chlorination was first reported in 1964 when coal was chlorinated in an aqueous media at 25°C. Only poor sulfur removal was achieved. Subsequent studies on desulfurization by gas phase chlorination of coal at high temperatures and elevated pressures resulted in better sulfur removals. However, the sulfur reductions were accompanied by higher coal losses and high chlorine retention in product coals.

Development of the chlorinolysis process for coal desulfurization began in 1976 at JPL. There are two basic variations of the process although both are based on the oxidation of sulfur by chlorine. The original version employed methyl chloroform as the reaction medium during chlorination, which was later substituted by water. A more recent version of the process consists of:

(1) Chlorination of an aqueous coal slurry (water:coal 2/1) at 60°C for 45 min (S/Cl_2 1/8 by wt).

(2) Filtration - wash of chlorinated coal (coal:water 1/2).

(3) Dechlorination of dry coal with N_2 at 400°C for 1 h.

(4) Advanced dechlorination with H_2 at 650°C for 1 h.[1]

The chemistry of the process is somewhat complex, but based on the sulfur bond scission in organic compounds, may be illustrated as follows:

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[1] This step enhances the total sulfur removal to the level of 90%.

9

The sulfur-chlorine bond and its chemical and physical properties are affected in a significant manner by unshared electron pairs and vacant d-orbitals on each atom. Both sulfur and chlorine have unshared electron pairs available for donation to another molecule. In addition, because sulfur and chlorine are second-row elements, they have empty d-orbitals that may be used to accept unshared electron pairs from other molecules. Molecules containing S-Cl bond may thus act as electrophiles or nucleophiles, depending on the circumstances.

The sulfur-chlorine reactions during chlorinolysis are summarized as follows:

1. Pyritic Sulfur

$$FeS_2 + 2Cl_2 \longrightarrow FeCl_2 + S_2 Cl_2$$
$$2\ FeS_2 + 7\ Cl_2 \longrightarrow 2\ FeCl_3 + 4\ SCl_2$$
$$2\ FeS_2 + 10\ SCl_2 \longrightarrow 2\ FeCl_3 + 7\ S_2Cl_2$$
$$S_2Cl_2 + 8\ H_2O + 5\ Cl_2 \longrightarrow 2\ H_2SO_4 + 12\ HCl$$
$$FeS_2 + 7\ Cl_2 + 8\ H_2O \longrightarrow FeCl_2 + 2H_2SO_4 + 12\ HCl$$
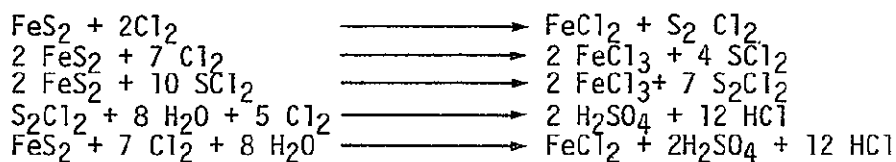
The overall reaction is assumed to proceed as:

$$2\ FeS_2 + 15\ Cl_2 + 16\ H_2O \longrightarrow 2\ FeCl_3 + 4H_2SO_4 + 24\ HCl$$
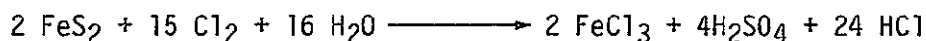
2. Organic Sulfur

C-S Bond Clevage:

$$R - S - R^1 + Cl^+ + Cl^- \underset{}{\overset{H^+}{\rightleftharpoons}} RSCl + R^1Cl$$
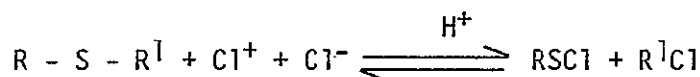
where R and R^1 represent hydrocarbon groups.

S-S Bond (electrophilic clevage)

$$RS - SR^1 + Cl^+ + Cl^- \underset{}{\overset{H^+}{\rightleftharpoons}} RSCl + R^1SCl$$
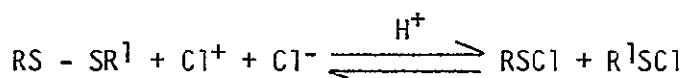
Oxidation of sulfenyl chloride to sulfonate or sulfate is assumed to proceed as:

$$RSCl \xrightarrow{Cl_2,\ H_2O} RSO_2Cl \xrightarrow{H_2O} RSO_3H + HCl$$

$$RSCl + 2\ Cl_2 + 3\ H_2O \longrightarrow RSO_3 H + 5\ HCl$$

or

$$RSCl \xrightarrow{Cl_2,\ H_2O} RSO_2Cl \xrightarrow[Cl_2,\ H_2O]{} SO_4^= + RCl$$

$$RSCl + 3\ Cl_2 + 4\ H_2O \longrightarrow RCl + H_2SO_4 + 6\ HCl$$
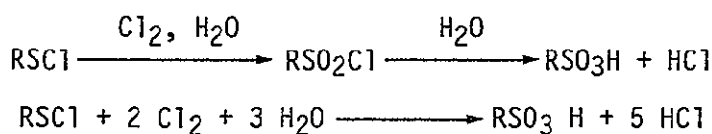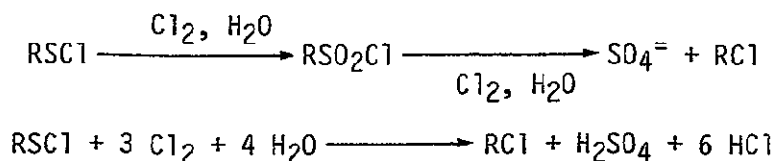
All these reactions are exothermic in nature and proceed favorably at low temperatures. In the presence of water and excess chlorine, sulfur dichloride is readily converted to sulfuric and hydrochloric acids.

B. COAL DESULFURIZATION IN THE SOLID PHASE

Coal desulfurization by treatment with different gases at elevated temperatures was reported by several investigators (Ref. 5 through 8). Early interest in such treatments was mainly for the production of metallurgical coke. Sulfur removal during carbonization was studied in both inert and reactive environments such as oxygen, hydrogen, steam, etc. Iron pyrites decomposes when heated, releasing half of its sulfur, while one-fourth to one-third of the organic sulfur is converted to hydrogen sulfide (Ref. 9 and 10).

Snow (Ref. 11) treated coal in various reactive gases and found hydrogen to be most effective. Pyrite reacts with hydrogen in two stages. The first stage of conversion of pyrite to ferrous sulfide begins at about 400°C while the subsequent reaction leading to the formation of elemental iron takes place at much higher temperatures. However, hydrodesulfurization of coal is strongly inhibited by the presence of hydrogen sulfide in the gas-phase (Ref. 12 through 14).

Treating coal with hydrogen at high temperatures (> 900°C) is very effective in the removal of organic sulfur, but the accompanying coal losses are substantial.

Several investigators have reported desulfurization of coal with oxygen and oxygen carriers and found that mainly pyritic sulfur was removed under the oxydizing atmosphere. One exception is the KVB or Guth process (Ref. 15) where the oxidation of sulfur compounds is brought about in the solid phase by using NO_2 followed by a caustic wash to remove up to 40% of organic sulfur. NO_2 is reported to selectively oxidize part of the pyritic and organic sulfur in coal. Block, et. al., (Ref. 16) reported that 87% pyritic sulfur was removed in a fluidized bed reactor at 600°C. Sinha and Walker (Ref. 17) reported that 90% of pyritic sulfur was removed in 10 min at 450°C while Jacobs and Mirkus (Ref. 18) in their studies on fluidized beds using steam-air mixtures found 60 to 70% sulfur reductions in 20 to 60 min at 510°C. Huang and Pulsifer (Ref. 19) found that the mechanism and extent of sulfur removal depends essentially on temperature and gaseous environment. At temperatures below 600°C desulfurization is achieved mainly by pyrolysis and release of volatile matter, while above 600°C hydrogen directly reacts with organic sulfur.

Thus, in principle, pyritic sulfur can be removed by oxidation and organic sulfur by reduction. However, neither of these methods is used to any great extent because of significant losses in coal heating value.

The earliest application of chlorine to remove sulfur from pyrites in the solid phase dates back to 1939 (Ref. 20). The authors reported an 85% removal of sulfur by treating FeS_2 with Cl_2 at 300 to 400°C. Another investigation claims that chlorine removes 95% of the sulfur from pyrites at 600°C (Ref. 21).

The present investigation was undertaken to study the feasibility of bringing about the desulfurization reactions in the solid phase by reacting gaseous chlorine with dry coal. Because the sulfur-chlorine reactions are exothermic, a fluidized bed reactor was chosen for the study as it is known to facilitate good solids mixing and isothermal operation. The main objectives of this investigation are:

(1) To study the effect of sequential chlorination, dechlorination and/or hydrodesulfurization of selected coals on total sulfur reductions in a fluidized bed reactor.

(2) To assess the influence of a wash of raw, chlorinated and desulfurized coals on the sulfur remaining in the product coals.

VII. LABORATORY SCALE COAL DESULFURIZATION EXPERIMENTS IN A BATCH-FLUIDIZED BED REACTOR

A. SELECTION OF COALS

Two bituminous high volatile coals were selected for the present study; PSOC 276 (Ohio No. 8) and PSOC 282 (Illinois No. 6). These were extensively studied in the laboratory-scale and bench-scale chlorinolysis experiments.

Five tons each of these coals obtained from the mine site as part of the earlier program, were ground and classified by the Corosil Corporation, Corona, California. For the laboratory scale experiments the ground coals were sieved to the required size, using a Sweco Vibro-Energy separator equipped with 60, 100 and 200 mesh stainless steel screens.

Results of sulfur forms and proximate and ultimate analyses by the ASTM approved methods at the Colorado School of Mines Research Institute are presented in Tables 1 and 2.

B. EQUIPMENT, OPERATING PROCEDURES AND METHODS OF ANALYSES

1. Equipment

A schematic of the experimental setup employed in the present study is shown in Figure 1. Figure 2 presents details of the fluidized bed reactor. The experimental set-up essentially consists of a preheater, reactor proper, reflux condenser and a scrubber, along with appropriate devices for measuring gas flows, and for controlling temperature.

The preheater, which is made of 1/2 in. I.D. x 30 in. stainless steel tube, is wound externally with a heating tape. One end of the preheater is connected to the reactor while the other end is connected to the gas inlet line. Temperature in the preheater is maintained at 50°C by a transformer, and the temperature is measured by a chromel-alumel thermocouple connected to a Hoskins Pyrometer.

The reactor is made of 1 in. I.D. x 24 in. quartz tube. A porous silica plate fused to the bottom end of the reactor serves as a gas distributor and support for the solids in the reactor. One end of the reactor is connected to the preheater while the other end is connected to solids disengaging section. The reactor is provided with a thermowell and tappings for pressure drop measurement. The bottom half of the reactor is enclosed in close fitting Thermcraft RH 212 Electric Heaters (264 W, 57.5 V). Temperature in the reactor was controlled by connecting the heaters and a Pt/Pt+13% Rh thermocouple to an OMEGA Model 49 ON-OFF Proportioning Temperature

Table 1. Characteristics of Raw-Coals Employed in the Studies

PSOC No.	Coal Type, Seam County, State	Size Tyler Mesh	Forms of Sulfur, wt%[a,b]				Total Sulfur, wt%[b,c]
			Organic	Pyritic	Sulfate	Total	
276	High Volatile, bituminous Pittsburgh coal from Harrison County, Ohio, George Town, No. 24 Mine	-60 + 100	1.17	2.63	0.06	3.87	3.75
282	High volatile, bituminous Illinois No. 6 coal from Jefferson County, Illinois, No. 6 Mine, (Washed)[d]	-60 + 100	0.75	0.43	0.36	1.54	1.58

[a] Determined by the Colorado School of Mines Research Institute (CSMRI).

[b] Dry basis.

[c] LECO analysis.

[d] Unwashed coal had 2.2 wt% total sulfur.

Controller. This was later replaced by a Wheel Co. Model 401 ON-OFF Temperature Controller. Temperature in the reactor was also recorded separately by means of an iron-constantan thermocouple connected to a Honeywell recorder.

The reactor outlet is connected to a reflux condenser for collecting any volatile components that may be present in the outlet gases.

The outlet gases from the reactor were scrubbed with 1 M Na_2CO_3 solution before they were finally vented into the atmosphere.

The reactor system after assembly was checked for leaks, flow-meter calibration, and satisfactory performance of heaters and temperature controller.

Table 2. Proximate and Ultimate Analyses of Raw Coals Employed in the Studies

Coal	Proximate Analysis, wt%[a]					Ultimate Analysis, wt%[a]						
	Volatile Matter	Fixed Carbon	Ash	Moisture[b]	Heating Value,[c] Btu/lb	C	H	S	N	cl[d]	O	Ash
PSOC 276	37.2	51.3	11.5	1.89	12,755	71.6	5.67	3.91	1.28	0.16	5.87	11.6
PSOC 282	33.8	59.5	6.70	3.10	13,092	74.8	4.82	1.60	1.69	0.47	9.92	6.70

[a]Dry basis.

[b]As determined basis.

[c]High heating value, dry basis.

[d]LECO Analysis gave 0.178% and 0.478% for PSOC 276 and PSOC 282 Coals, respectively.

15

R REGULATOR

V MANUAL VALVE

F FLOW METER

SJ STANDARD
    GLASS JOINT

BS BALL AND
    SOCKET JOINT

VENT

LEGEND

1. CHLORINE CYLINDER
2. NITROGEN CYLINDER
3. HYDROGEN CYLINDER
4. PREHEATER (1/2" ID x 30" SS TUBE)
5. HEATING.TAPE
6. TEMPERATURE INDICATOR
7. TEMPERATURE INDICATOR CUM
    ON-OFF CONTROLLER
8. SWEGE-LOCK JOINT

9. ELECTRICAL HEATERS
10. REACTOR
11. POROUS SILICA
    DISTRIBUTOR
12. THERMOCOUPLE
13. MANOMETER
14. REFLUX CONDENSER
15. RECEIVING FLASK
16. SCRUBBER
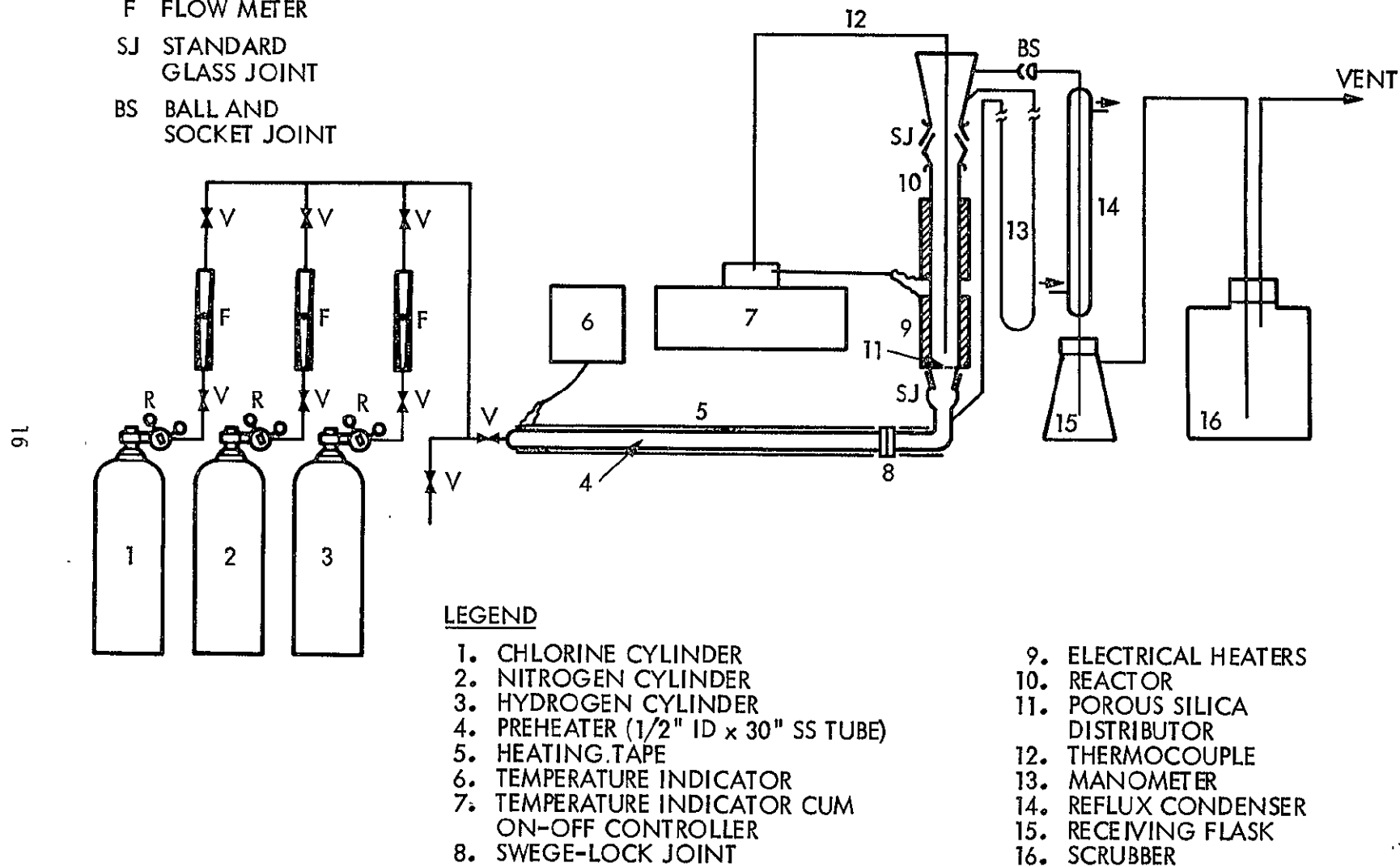
Figure 1. Batch Fluidized Bed Reactor System for Coal Desulfuization

4 "

THERMOCOUPLE
ENTRY POINT

MANOMETER
TAPPING

6"

1" QUARTZ TUBE

18"

SUPPORT FOR
HEATER

MEDIUM POROSITY
SINTERED SILICA
DISTRIBUTOR

MANOMETER
TAPPING

4"

1/2"
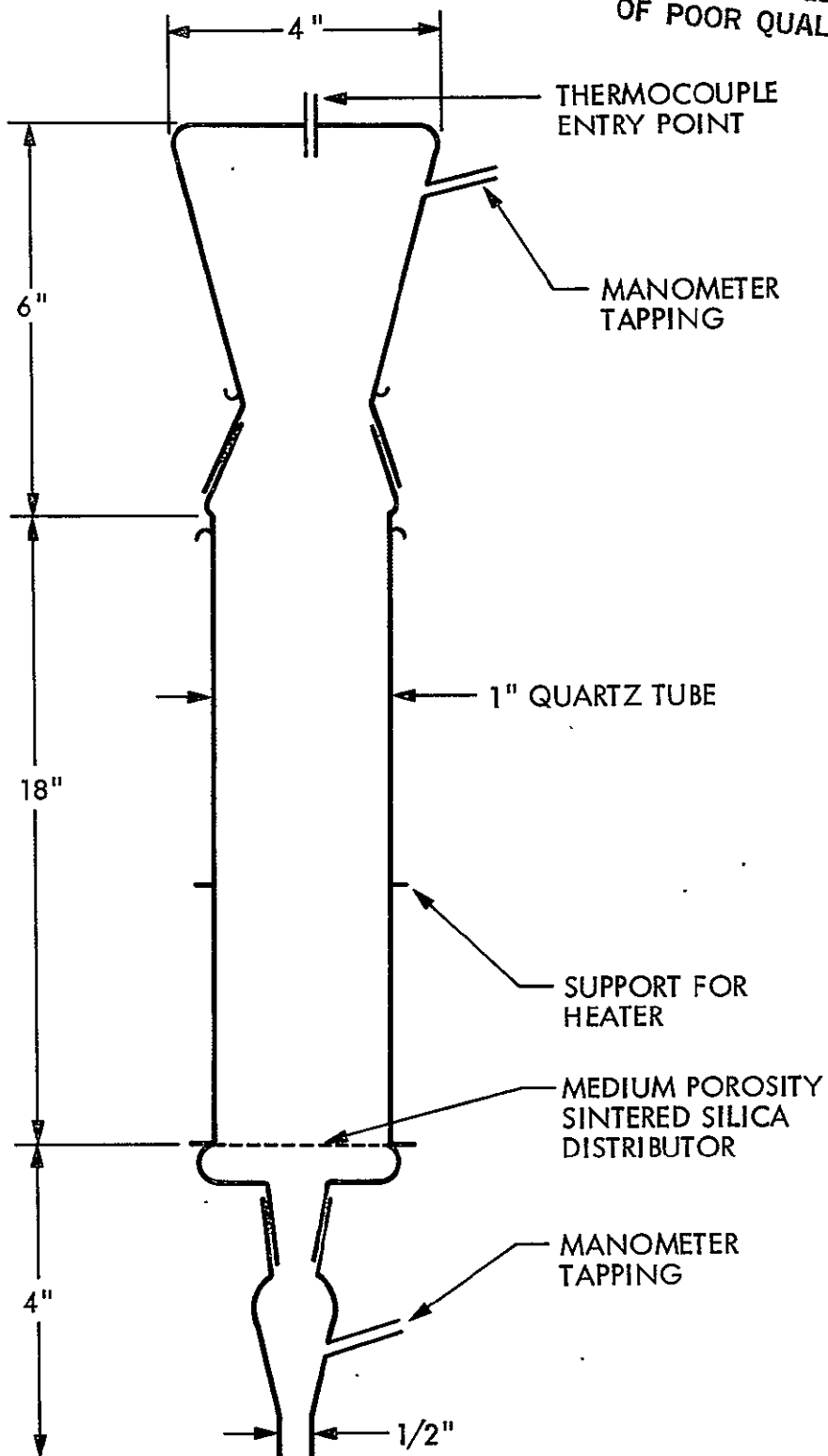
Figure 2.   Fluidized Bed Reactor

2. Fluidization Experiments

Initially, fluidization characteristics of coal were assessed. For this purpose graded sizes (-60 + 100 and -100 + 200 Mesh) of PSOC 276 and PSOC 282 coals were employed in the fluidization experiments. 50 g of dry coal of a known particle size were taken in the reactor and the flow rate of nitrogen was gradually increased. The onset of fluidization and solids mixing in the reactor were visually observed. Pressure drop and bed expansion at each flow rate were noted. A constant pressure drop and vigorous mixing of solids in the bed were taken as indicative of fluidization. The pressure drop was also noted while the flow rate was decreased. The experiments were repeated using hydrogen as the fluidizing medium. Representative plots of pressure drop versus volumetric flow rate are presented in Figures 3 and 4. The minimum fluidization velocity was also calculated using the following equation applicable for small particles.

$$U_{mf} = \frac{dp^2 \; (\rho_s - \rho_g) \; g}{1650\mu}$$

where,

U_{mf} = minimum fluidization velocity, cm/s

dp = mean particle diameter, cm

ρ_s = solids density, g/cm^3

ρ_g = fluid density, g/cm^3

g = local acceleration due to gravity, cm/s^2

μ = fluid viscosity, g/cm s

From the minimum fluidization velocity the corresponding volumetric flow rate was calculated as follows:

$$Q = U_{mf} \times A$$

where,

Q = volumetric flow rate, cm^3/s

A = cross sectional area of the bed, cm^2

18
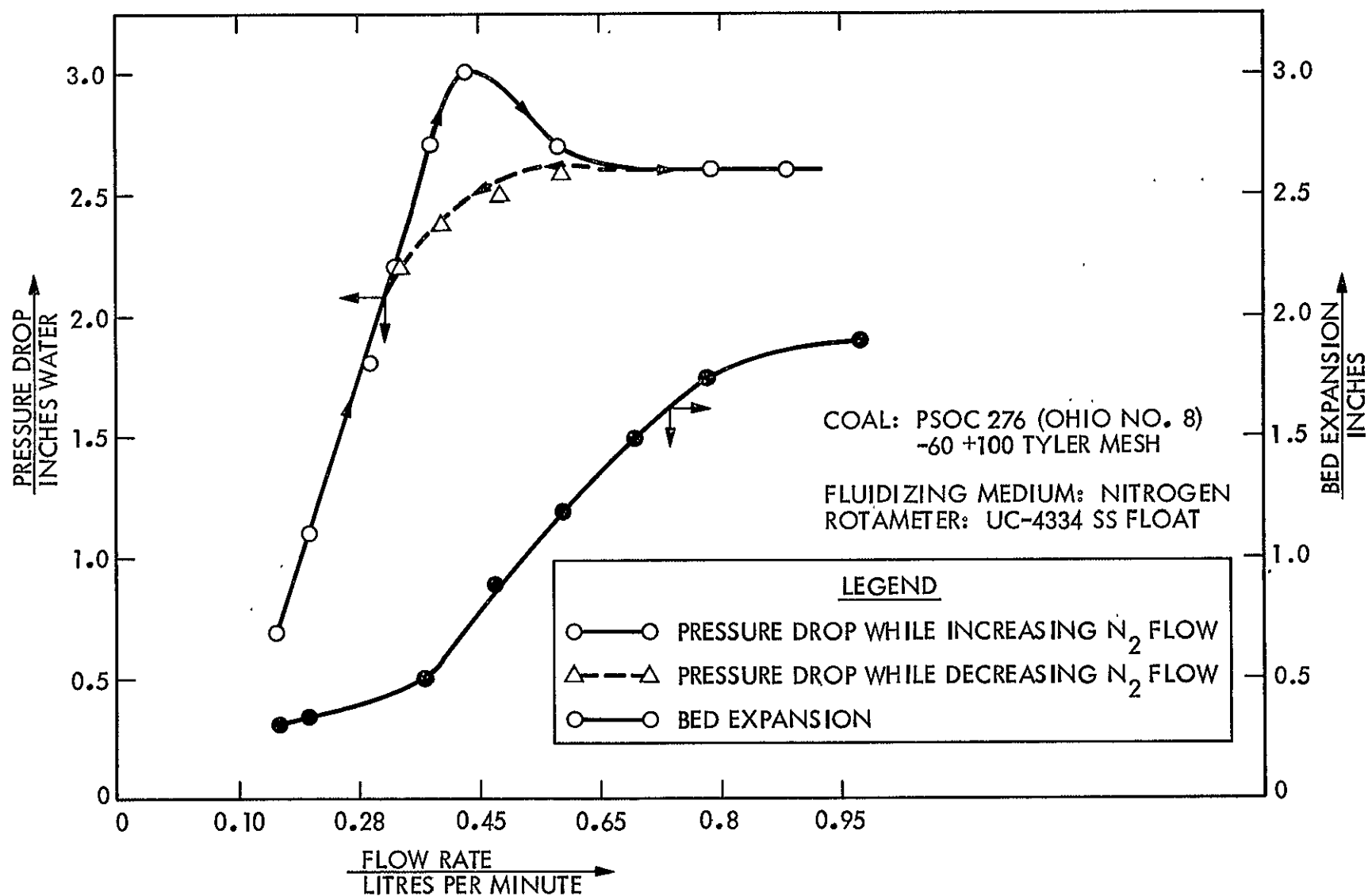
Figure 3. Fluidization Characteristics of Coal
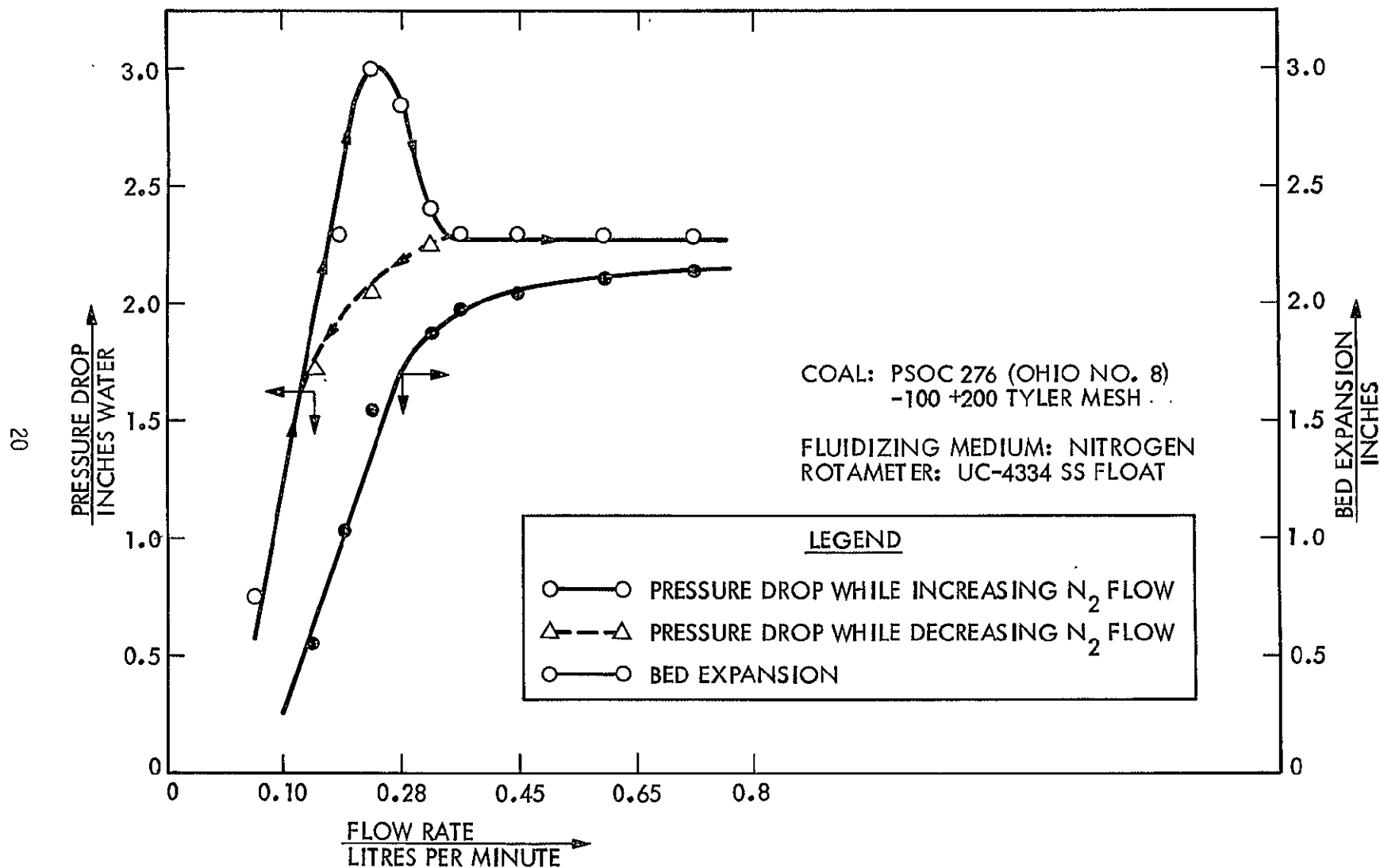
Figure 4. Fluidization Characteristics of Coal

20

The minimum fluidization velocities calculated using the above equation and those computed from pressure drop data are presented in Table 3. For the size fractions employed, there was no significant carryover of coal particles in the exit stream. The actual flow rates employed in the desulfurization experiments are presented in Table 4.

3.   Desulfurization Experiments

The desulfurization experiments consisted of successive chlorination, dechlorination and/or hydrodesulfurization of selected coals for varying time intervals and temperatures in the fluidized state. The effect of employing a mixture of nitrogen and chlorine (4:1) and pre- and post-treatments to coals were also assessed. A process flow diagram of the treatments is presented in Figure 5.

The experimental procedure is as follows: 50 g of coal of the required particle size are loaded into the reactor and fluidized with nitrogen. After ensuring that the entire system is functioning properly and the preheater has reached the required temperature, the chlorination experiment is started by substituting chlorine as the fluidizing medium at the predetermined flow rate. During the initial stages of chlorination, the temperature of the bed rose sharply. However, the vigorous mixing of the solids in the reactor prevented local hot spots. With proper insulation the reactor temperature could be maintained uniformly at about 100°C without supplying any additional heating. During preliminary runs using coal as received (without drying) it was observed that the bed tends to consolidate as a consequence of the exothermic sulfur-chlorine reaction, resulting in defluidization and pressure buildup in the reactor. This problem was overcome by employing dried coal (dried at 100°C overnight) in all the subsequent experiments. The chlorination experiments lasted from 5 to 15 min. Unreacted chlorine and the products of chlorine-sulfur reactions are absorbed in 1 M Na_2CO_3 solution in the scrubber.

After chlorination, nitrogen is substituted as the fluidizing medium and the reactor temperature is set to the required level. After the reactor attained the required temperature (400 to 600°C), dechlorination is carried out for time intervals varying from 10 to 60 min.

For the hydrodesulfurization step, the reactor temperature is set to the required level while still being fluidized with nitrogen. After the reactor attained the required temperature, hydrogen is substituted as the fluidizing medium and the hydrodesulfurization of coal is carried out for time intervals ranging from 10 to 30 min in the temperature range of 500 to 700°C.

After completing the hydrodesulfurization experiment, the heaters are switched off, hydrogen flow is stopped and nitrogen is once

Table 3. Calculated and Observed Values of Minimum Fluidization Velocity, U_{mf}

Size Fraction Tyler Mesh	Mean Particle Diameter, cm	Calculated U_{mf}, cm/s			Observed U_{mf}, cm/s			
					Nitrogen		Hydrogen	
		N_2	Cl_2	H_2	PSOC 276	PSOC 282	PSOC 276	PSOC 282
-60 + 100.	0.01995	1.99	2.68	3.98	1.81	2.14	2.72	2.72
-100 + 200	0.01115	0.62	0.84	1.26	0.76	0.79	1.03	1.03

Table 4. Actual Flow Rates Employed in the Experiments, -60 + 100 Tyler Mesh

Fluidizing Gas	Flow Rate, 1/min
Chlorine	0.610
Nitrogen	0.600
Hydrogen	0.900

DRY, POWDERED COAL →

CHLORINATION •
50–100°C, 1 ATM
5–15 MIN
FLUIDIZED BED REACTOR

CHLORINE GAS →

SCl_2, S_2Cl_2 →
Cl_2, HCl (g) →

CHLORINATED COAL

WASHING-DRYING *
AMBIENT, 1 ATM
30 MIN

WATER/Na_2CO_3 →

WASTE WATER
INCLUDING HCl,
H_2SO_4, SOLUBLE
SULFATES AND CHLORIDES/
SODIUM SULFIDE, SULFATE, etc.

DECHLORINATION •
300–500°C, 1 ATM
10–60 MIN
FLUIDIZED BED REACTOR

NITROGEN →
HCl (g) →

HYDRODESULFURIZATION •
500–700°C, 1 ATM
10–60 MIN
FLUIDIZED BED REACTOR

HYDROGEN →
H_2S →

WASHING AND DRYING *

WATER/Na_2CO_3 →

H_2SO_4, SOLUBLE SULFATES
SULFIDES etc.

DESULFURIZED COAL

• LABORATORY GLASS EQUIPMENT FOR THESE PROCESSES
IS SHOWN IN FIGURE 1

* OPTIONAL

Figure 5. Process Flow Diagram for Laboratory Scale Fluidized
Bed Coal Desulfurization

23

again substituted as the fluidizing medium. The reactor is cooled to room temperature in a nitrogen atmosphere.

After the experiment, the reactor is disconnected from the system and the reacted coal is collected and stored for subsequent analyses.

In some cases, raw coal, chlorinated coal, and product coal are subjected to a washing treatment consisting of water wash and carbonate wash. For a water wash, the sample is soaked in distilled water with occasional stirring for 30 min after which the coal is filtered and dried overnight at 100°C. In a carbonate wash, the sample is soaked in 1 M Na_2CO_3 solution for 30 min with frequent stirring, after which the coal is filtered, washed repeatedly till the washings are neutral to litmus and dried at 100°C overnight.

A safety and operating procedure for the fluidized bed coal desulfurization experiments is presented in Appendix A.

4.   Methods of Analysis

   a.   Analysis of Sulfur Forms in Coal

        Raw coals and some of the processed coals were analyzed for sulfur forms by ASTM approved methods at the Colorado School of Mines Research Institute. Appendix B gives the details of analysis methods.

   b.   Proximate and Ultimate Analyses of Coal

        Selected desulfurized coal samples were submitted to the Colorado School of Mines Research Institute for long proximate and ultimate analyses by ASTM-approved methods.

   c.   Estimation of Total Sulfur in Coal

        Processed coals immediately after the desulfurization experiments were analyzed by a modified LECO Method for total sulfur. Details of the method are given in Appendix C. This routine analysis in the laboratory provided a rapid estimation of the total sulfur needed for planning further experiments.

        A more complete analyses for total sulfur and sulfur forms were carried out by CSMRI as indicated in (a) and (b) above. During the earlier work in this laboratory it was observed that the estimations of total sulfur by LECO and the Eschka methods were in general in good agreement, as shown in Table 5.

24

Table 5. LECO Acid-base Analysis vs. Eschka[a] Analysis for Total Sulfur

Run No.[b]	Total Sulfur by LECO, wt%	Total Sulfur by Eschka, wt%	Difference LECO - Eschka
B14	1.42	1.54	-0.12
L2	1.56	1.54	+0.02
B17	1.48	1.54	-0.06
L9	1.31	1.54	-0.23
L42	0.48	0.57	-0.09
B22	0.72	0.88	-0.16
B38	1.72	1.58	+0.14
L30	0.63	0.61	+0.02
L38	0.22	0.29	-0.07
L44	1.24	1.22	+0.02
L48	0.53	0.55	-0.02
L49	0.78	0.78	0.00

[a] Conducted by CSMRI.

[b] From Phase III Report (Ref. 3).

d. Surface Area and Pore Volume of Coal

Specific surface area and pore volume of raw coals were
determined by low-temperature nitrogen adsorption employing a
Quantasorb Sorption System. Surface area and pore volume were
calculated by applying the BET equation as described in
Appendix D. The results are presented in Table 6. While the
surface areas of raw coals appear to be low, it is generally
observed that employing nitrogen as an adsorbate results in
the estimation of low surface areas as compared to carbon
dioxide, due to the presence of a majority of micropores in
coal. In addition, it was reported that during desulfuriza-
tion new pores are created in coal, resulting in a pronounced
increase in the surface area of processed coals.

e. Analysis of Scrubber Solution

In an attempt to estimate the amount of sulfur removed as
gaseous species along with the reactor outlet gases, the
scrubber solution after the experiment was analyzed in some
instances by precipitating $BaSO_4$. However, total sulfur
estimated by this method accounted to only 20% of that
estimated by the LECO analysis of product coals. The apparent
discrepancy might be due to the nature of sulfur species
present in the outlet gases and their decomposition rates.

It is known that chlorine gas readily reacts with pyrite,
forming ferrous chloride and sulfur monochloride ($S_2 Cl_2$)
as follows:

$$Fe S_2 + 2 Cl_2 \longrightarrow Fe Cl_2 + S_2 Cl_2$$
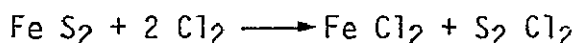
In the presence of excess chlorine the products of reaction
are ferric chloride and sulfur dichloride as given by the
following equation:

$$2 Fe S_2 + 7 Cl_2 \longrightarrow 2 Fe Cl_3 + 4 SCl_2$$
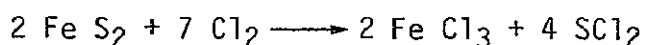
Sulfur monochloride is quite stable at room temperatures, but
a reversible breakdown starts at about 100°C and beyond 300°C
complete breakdown takes place as:

$$S_2 Cl_2 \rightleftharpoons S_2 + Cl_2$$
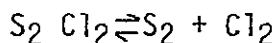
Sulfur monochloride is slowly hydrolysed by water at room
temperature as follows:

$$S_2 Cl_2 + 2 H_2O \longrightarrow 2 HCl + SO_2 + H_2S$$
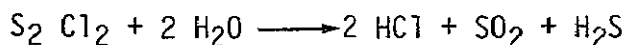
In solution, SO_2 and H_2S further react to form elemental
sulfur and polythionic acids. However, in the presence of
excess chlorine, $S_2 Cl_2$ decomposes, forming sulfuric and
hydrochloric acids as:

26

Table 6. Specific Surface Area and Pore Volume of Raw Coals
Employed in the Study

Coal	Size Fraction Tyler Mesh	S_g, Specific Surface Area, m^2/g	V_g, Pore Volume, cm^3/g	Y_m Mean Pore Diameter[a] A
PSOC 276	-60 ÷ 100	7.20	0.0160	44.5
PSOC 282[b]	-60 ÷ 100	6.01	0.0127	43.6

[a] For a Spherical Pore, $Y_m = \dfrac{2 \times V_g}{S_g}$.

[b] Fuller, Jr., E. L. (ACS Advances in Chemistry Series, Vol. 192, 1961) reported a BET surface area of 2.6 m^2/g by nitrogen adsorption for a bituminous Illinois No. 6 coal from Sahara Mine, whereas the same coal by carbon dioxide adsorption gave a surface area of 128 m^2/g.

$$S_2 Cl_2 + 5 Cl_2 + 8 H_2O \longrightarrow 2 H_2 SO_4 + 12 HCl$$
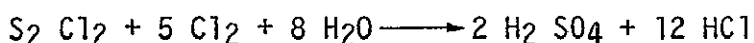
As the scrubber solution contains Na_2CO_3, H_2S is likely to react forming Na_2S as follows:

$$Na_2 CO_3 + H_2S \longrightarrow Na_2S + CO_2 + H_2O$$
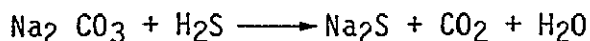
Sulfur dichloride also undergoes similar hydrolysis reactions and is readily decomposed on contact with water.

The complex series of reactions taking place may be the reason for underestimating sulfur removal in the process by the analysis of scrubber solution for SO_4.

f. Coal Characterization Using Scanning Electron Microscopy (SEM)

An examination of the microstructure of coal is of interest in understanding its properties. Details of size, shape, orientation and distribution factors for pyrite, certain pyrite and marceral groupings or other coal constituents (such as mineral matter) are useful in supporting coal cleaning processes. Recent studies on coal structure using Scanning Electron Microscopy (SEM) have shown that interrelationships exist between marcerals and inorganic phases such as FeS_2. This form of characterization complements optical microscopy and conventional transmission electron microscopy (TEM) that have been used to classify and study coal constituents.

SEM offers a means of visualizing features hundreds and thousands of Angstroms in diameter in a three dimensional form that is not available by any other technique. Although the nature of coal surface precludes any precise quantitative measurements with SEM, useful qualitative conclusions could be drawn regarding the effect of various treatments on the gross structural properties of coal.

By using SEM equipped with an Energy Dispersive X-ray Analysis (EDAX) system, microscale structural and chemical analysis of coal could be achieved. A more detailed description of the applicability of these methods can be found in Reference 22.

The SEM and EDAX of raw and product coal particles were examined using AMR (Advanced Metals Research Corporation) Model 900 SEM fitted with EDAX Model XC-12-164.

The images of the particles were obtained using secondary electrons. Because coal is a light element composed primarily of carbon, the electrons in the impinging beam interact more diffusely with coal than with a metal. Consequently, it becomes much harder to obtain a sharp image at higher magnifications. Therefore, best resolution is normally obtained at about 1000 Å whereas most of the coal pore structure is composed of micropores (less than 15 Å).

28

In addition to the production of backscattered electrons, the interaction of the impinging electron beam also yields x-rays. There are two electron beam-solid interactions that lead to the production of x-rays: (1) core-scattering, which results in the emission of a continuous spectrum; and (2) inner shell ionization, which yields the characteristic spectrum. The characteristic spectrum allows the qualitative identification of the elements present in the sample. The basic function of EDAX is to collect all of the x-rays produced, analyze their energies, and present the results in a convenient form on a Cathode ray tube. The EDAX is calibrated using the x-rays generated by aluminum and zirconium or zirconium and gold to fix the energy scale. Once calibrated, the element corresponding to any peak can be readily identified. A facsimile of some typical EDAX spectra are shown in Figure 6. For any given sample, usually 15 to 25 separate particles were examined, and the picture of the most representative one was taken. The EDAX spectra usually requires about 100 to 1000 seconds of data acquisition to yield an acceptable signal to noise ratio. The SEM photographs and EDAX spectra of raw and processed coals are presented in Figures 7 to 14 and 15 to 18, respectively.
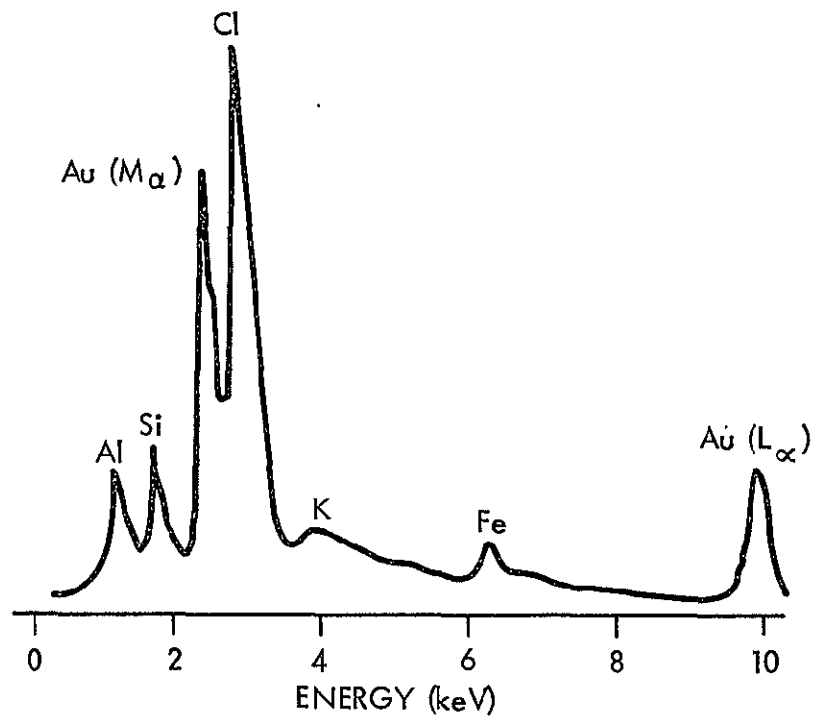
A HIGHLY CHLORINATED COAL
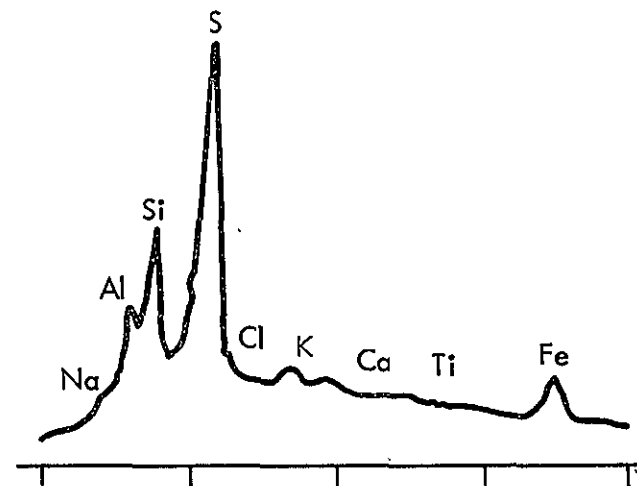
A HIGH SULFUR BITUMINOUS COAL

Figure 6. Typical EDAX Spectrum of Coal

1 μm
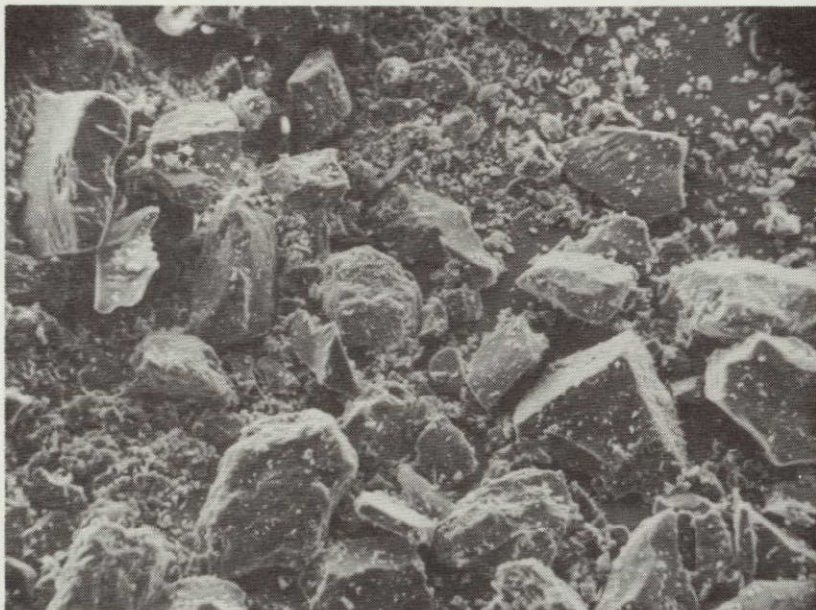
100 μm

Figure 7. SEM Photograph of PSOC 282 Raw Coal

31

1 μm
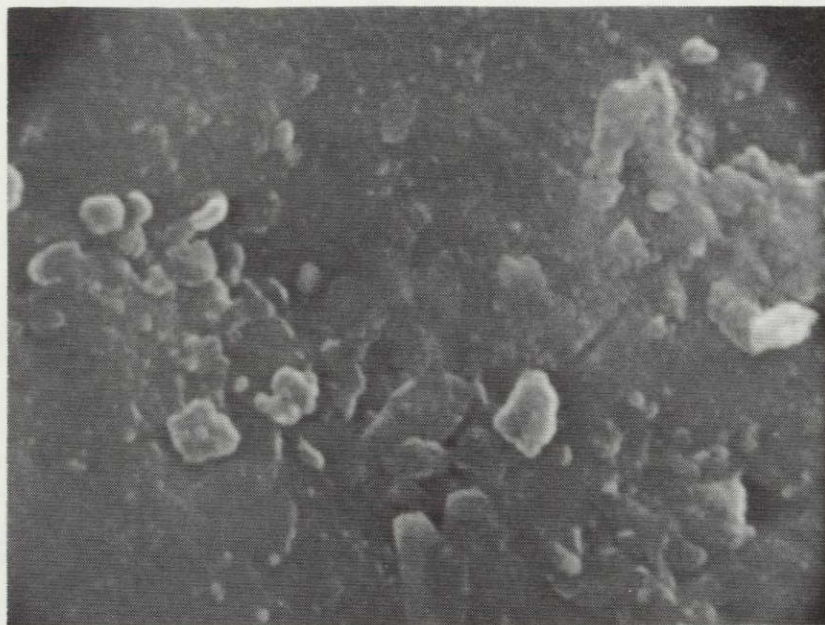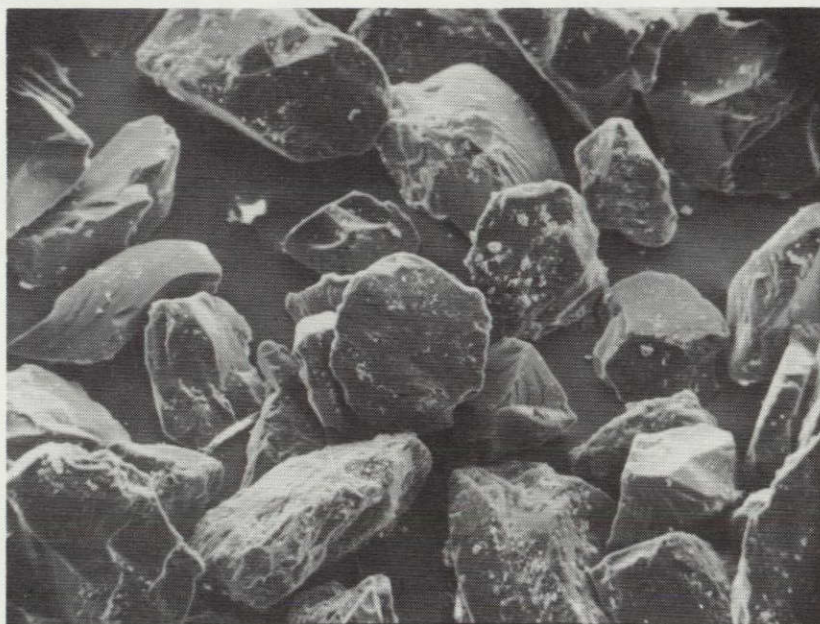
100 μm

Figure 8. SEM Photograph of PSOC 282 Washed with
1 M Na_2CO_3 Solution

1 μm
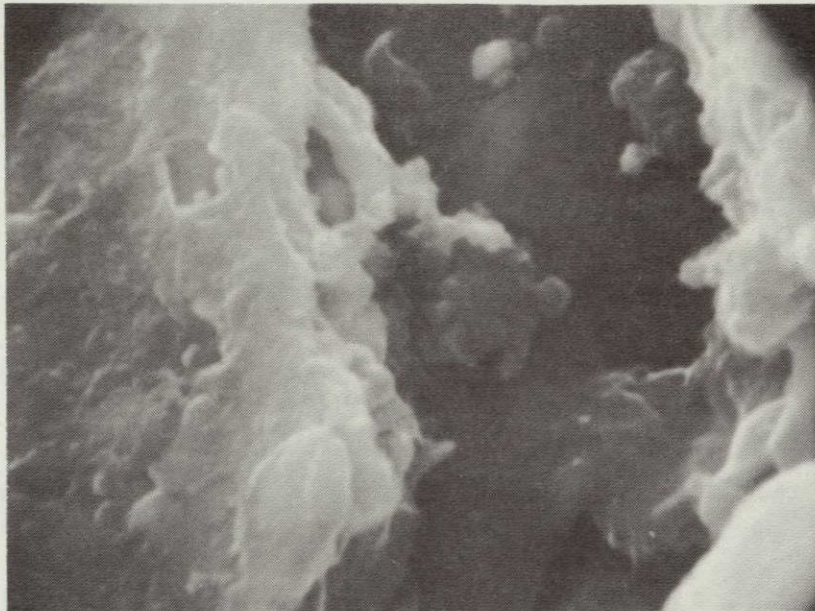
100 μm

Figure 9. SEM Photograph of PSOC 282 Treated Coal
(Run No. 0032)

33

1 μm
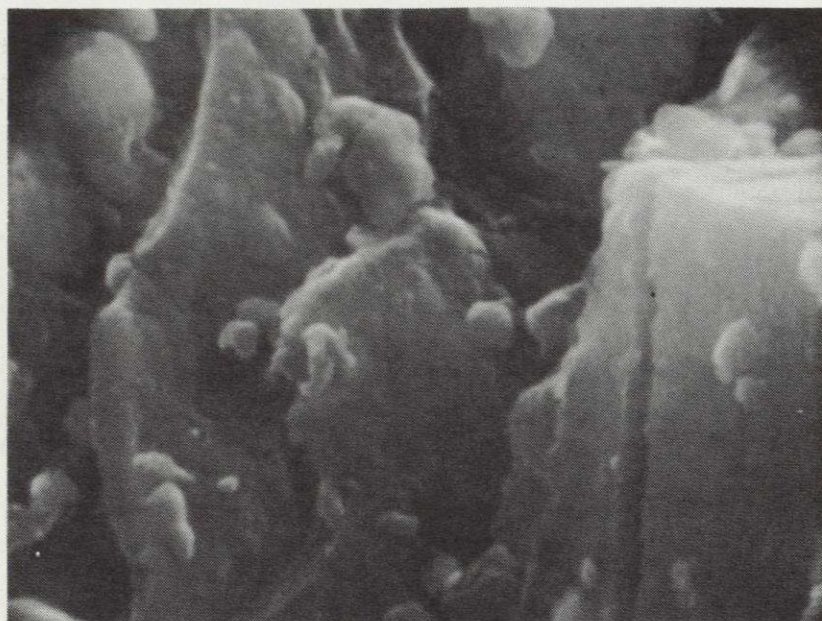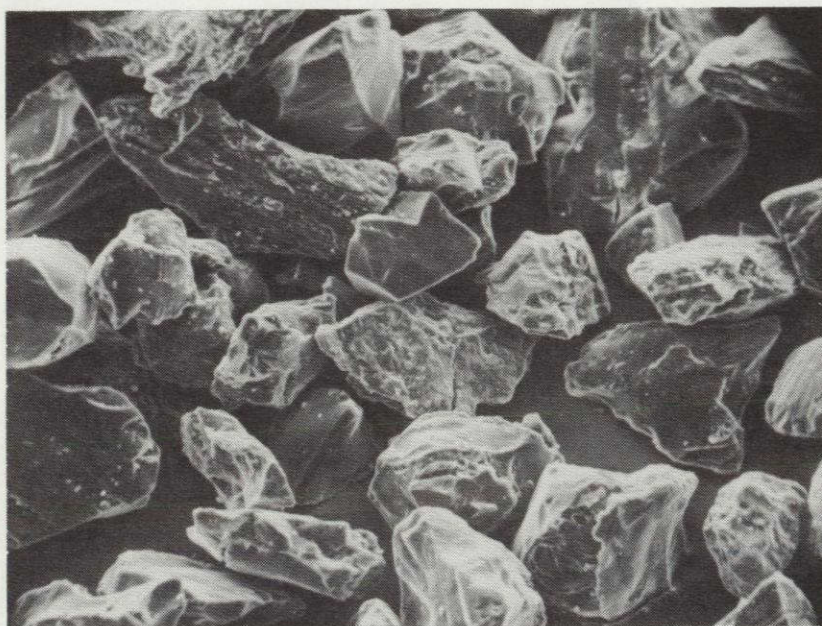
100 μm

Figure 10. SEM Photograph of PSOC 282 Treated Coal
(Run No. 0026)

34

1 μm
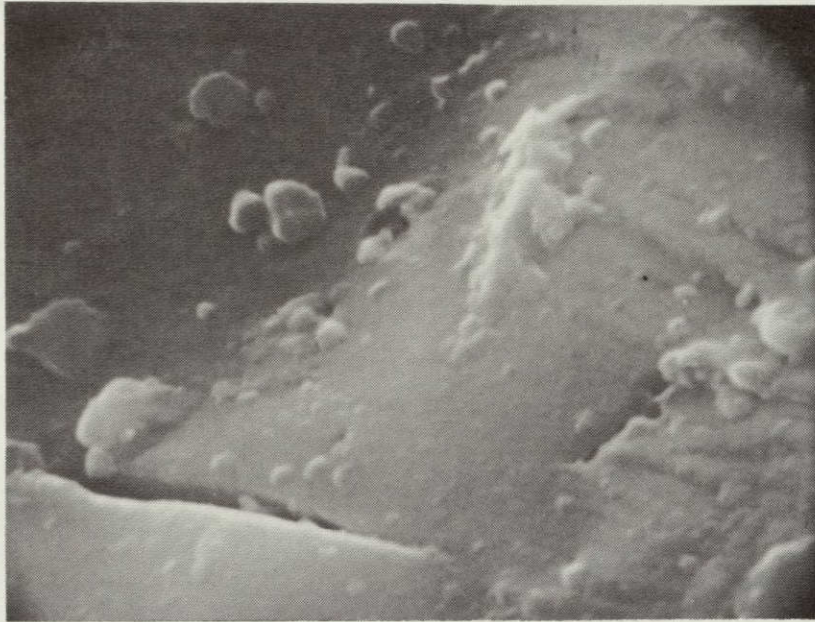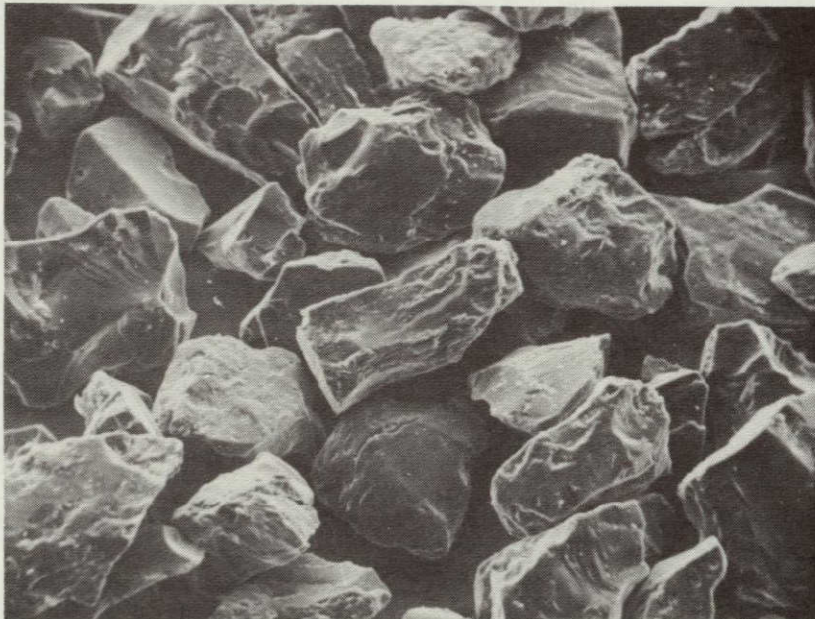
100 μm

Figure 11.   SEM Photograph of PSOC 282 Treated Coal
(Run No. 0027)

35

1 μm
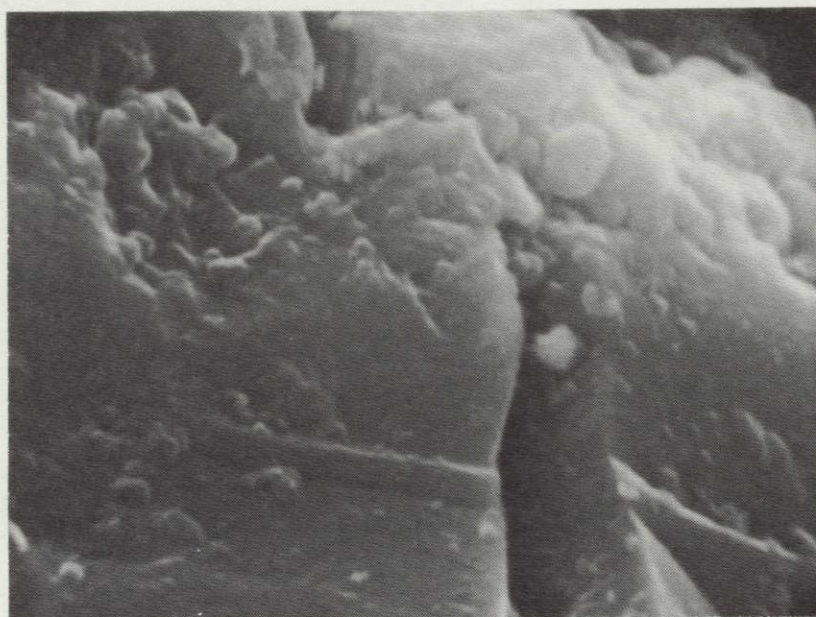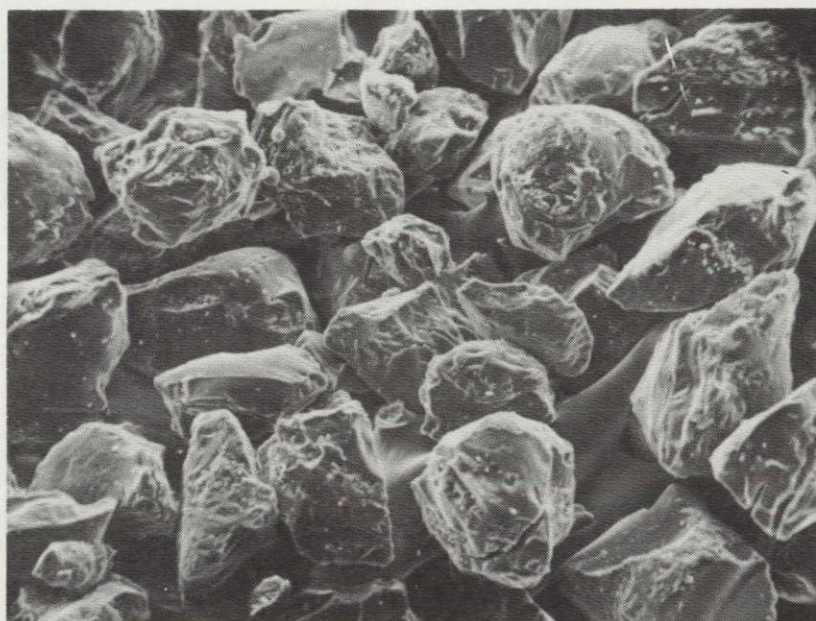
100 μm

Figure 12. SEM Photograph of PSOC 282 Treated Coal
(Run No. 0039)

1 μm
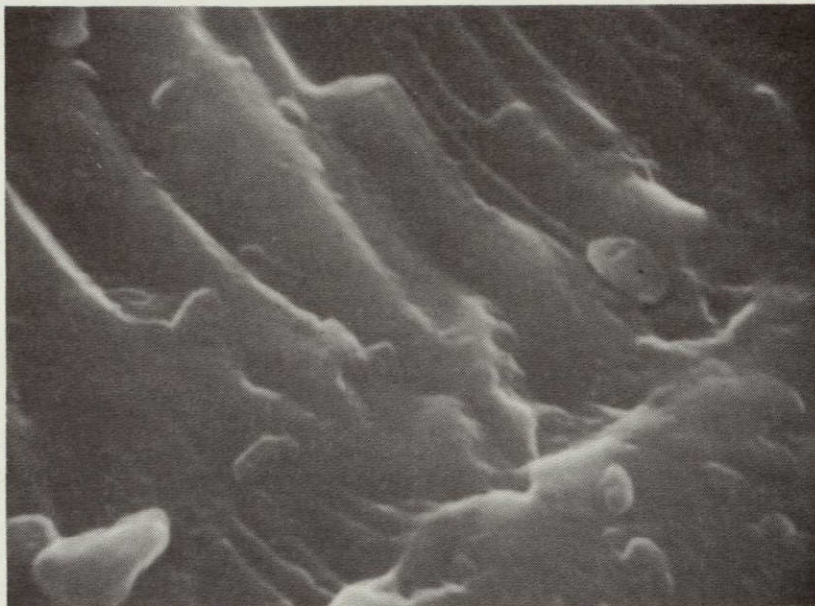
100 μm

Figure 13.   SEM Photograph of PSOC 276 Raw Coal

37

| |
1 μm
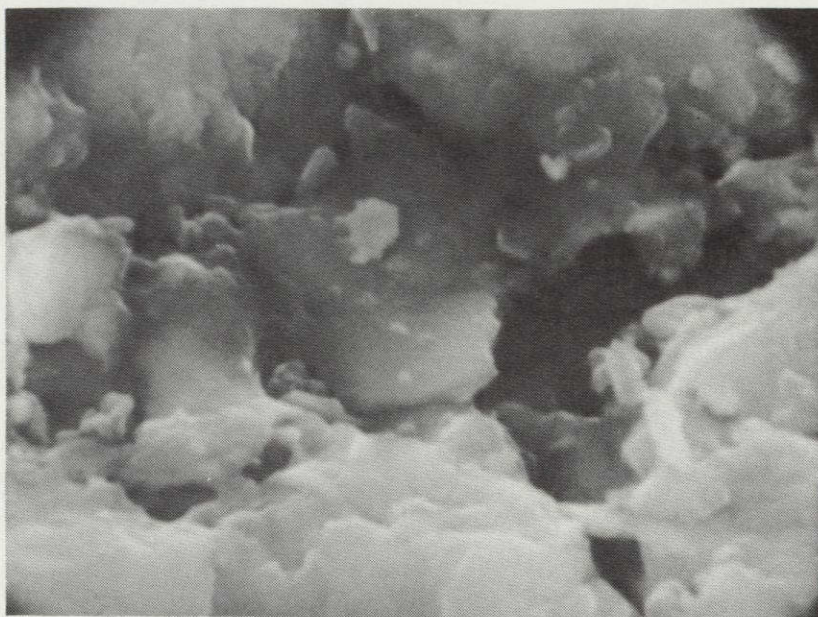
| |
100 μm

Figure 14. SEM Photograph of PSOC 276 Treated Coal
(Run No. 0046)
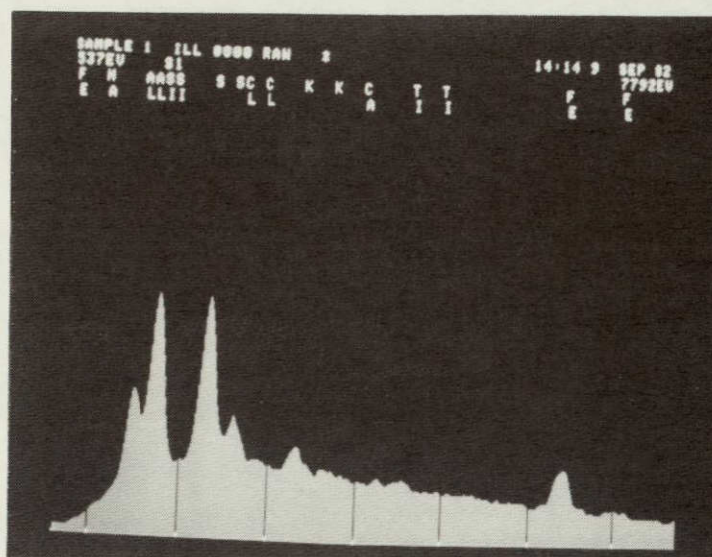
PSOC 282 RAW COAL
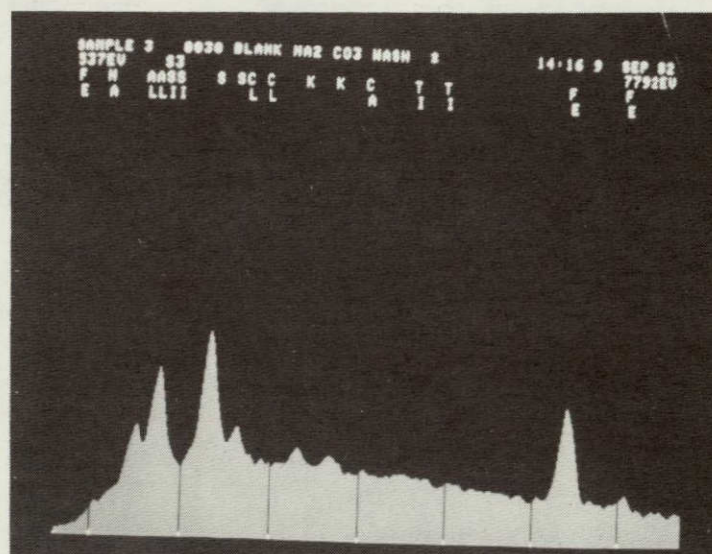
PSOC 282 COAL WASHED WITH IM Na_2CO_3 SOLUTION

Figure 15. EDAX Spectrum of Coal

39
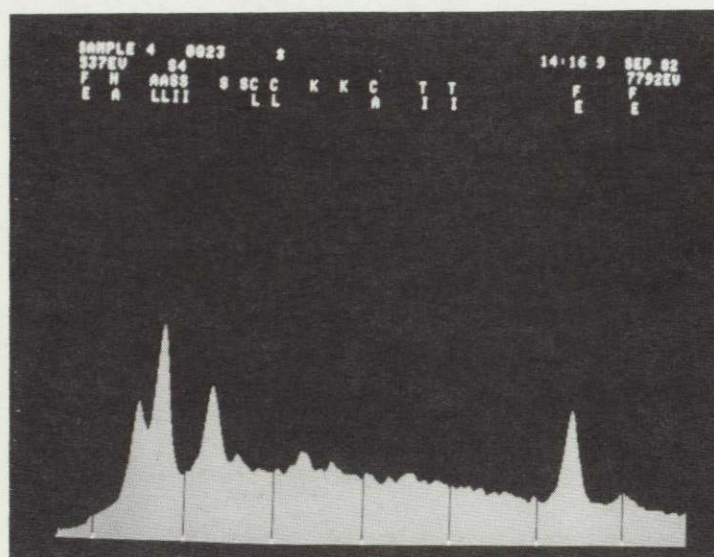
PSOC 282 TREATED COAL (RUN NO. 0023)
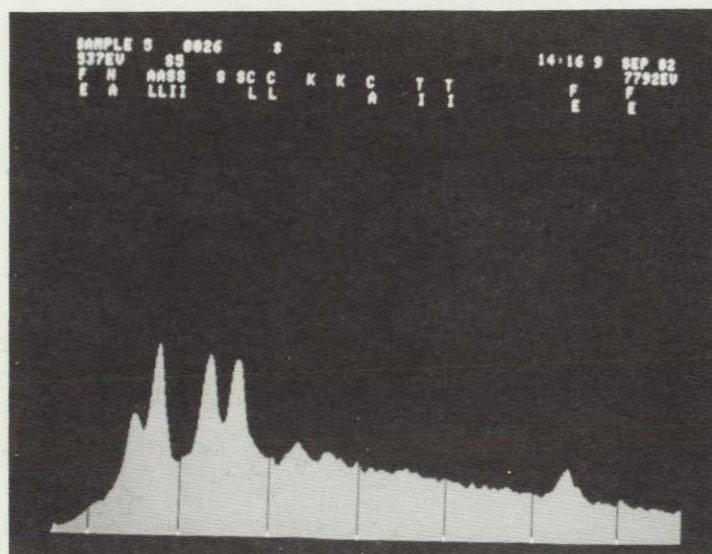
PSOC 282 TREATED COAL (RUN NO. 0026)

Figure 16. EDAX Spectrum of Coal

40
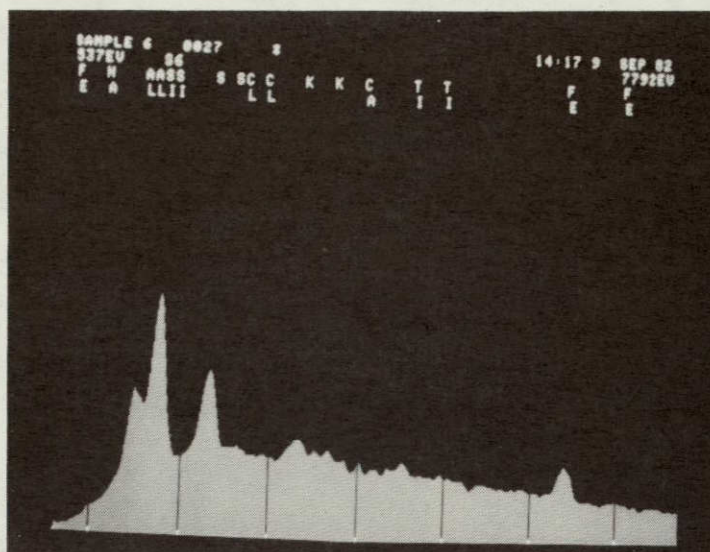
PSOC 282 TREATED COAL (RUN NO. 0027)
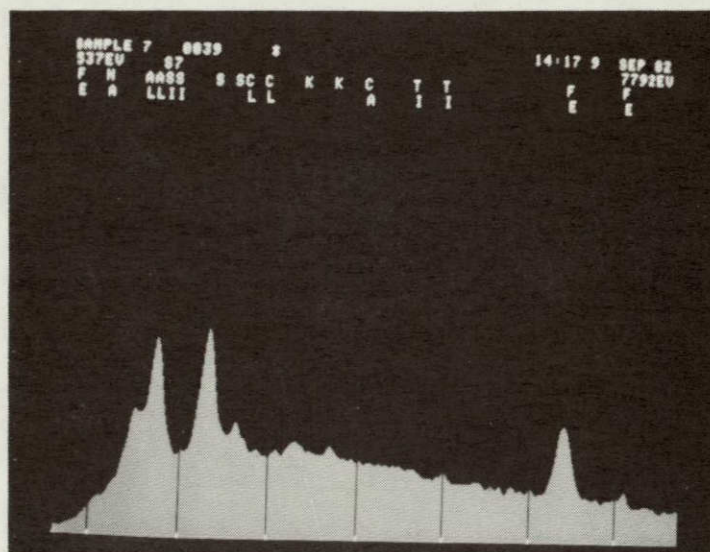
PSOC 282 TREATED COAL (RUN NO. 0039)

Figure 17. EDAX Spectrum of Coal

41
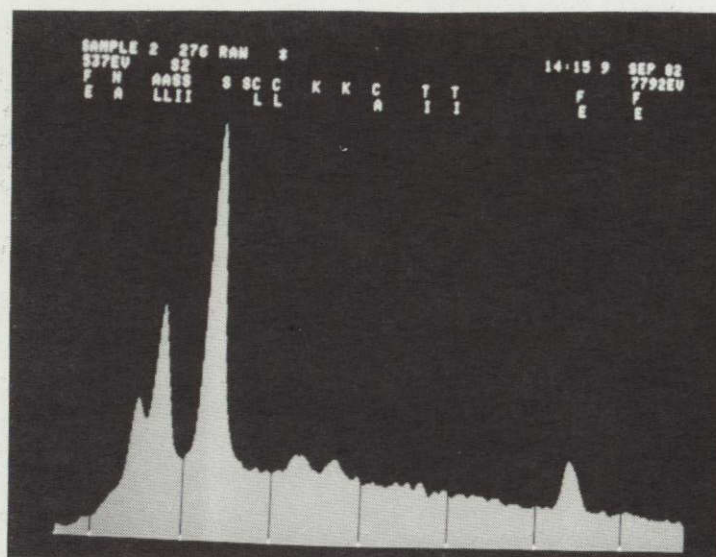
PSOC 276 RAW COAL
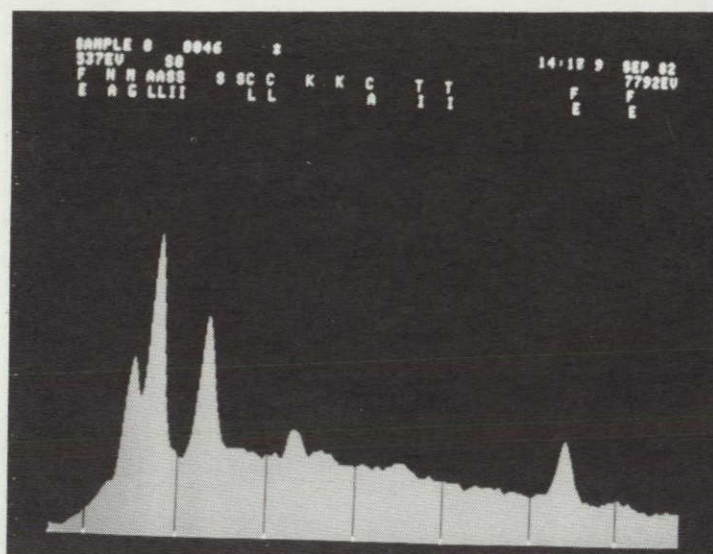
PSOC 276 TREATED COAL (RUN NO. 0046)

Figure 18. EDAX Spectrum of Coal

VIII. RESULTS AND CONCLUSIONS

Fluidized bed coal desulfurization experiments were conducted employing PSOC 276 and PSOC 282 coals. A total of 26 experiments were conducted to investigate the effects of: (1) chlorination, dechlorination and hydro-desulfurization as a function of reaction time and temperature; (2) pre- and post-treatment of raw and processed coals; and (3) changing chlorine concentration during chlorination, on total sulfur reductions in coals. The ranges of variable studied are as follows:

(1) Coal type: PSOC 276 and PSOC 282.

(2) Particle size: -60 + 100 and -100 + 200 Tyler Mesh.

(3) Chlorination time: 5 to 15 min.

(4) Chlorination temperature: Approximately 100 to 250°C.

(5) Chlorine concentration: Pure chlorine and a mixture of 1:4 chlorine and nitrogen.

(6) Dechlorination time: 10 to 60 min.

(7) Dechlorination temperature: 300 to 500°C.

(8) Hydrodesulfurization time: 10 to 30 min.

(9) Hydrodesulfurization temperature: 500 to 700°C.

(10) Pre- and post-treatments to Coal: These consisted of carbonate wash of chlorinated and product coals.

Experimental conditions and results in the form of total sulfur estimation by LECO Analyses are presented in Tables 7 and 8. The results are also depicted in Figures 19 and 20. Results of a complete analysis of selected coals carried by CSMRI are presented in Section X of this report (see Tables 9 through 12).

A. PSOC 282 COAL

A total of 20 experiments were conducted to assess the influence of various process parameters on the extent of desulfurization in the fluidized bed reactor.

A maximum level of 74% desulfurization (Runs 0021 and 0027) was achieved in the process based on 1.581% total sulfur in the raw coal. However, based on the sulfur content of unwashed coal (2.2% total sulfur) the level of desulfurization was 81%.

43

Table 7. Experimental Condition and Results

COAL: PSOC 282, Illinois No. 6 (-60 + 100 Tyler Mesh)   Total Sulfur: 1.581 (Wt%)[a]

Experiment No.	Chlorination	Intermediate Wash	Dechlorination with Nitrogen	Advanced Dechlorination with Hydrogen	Post-Treatment	% Total Sulfur in Product[a]	% Desulfurization
0001	15 min, ambient	-	30 min, 400°C	-	-	1.170	26.1
0002	15 min, ambient	-	30 min, 400°C	-	water wash	1.082	31.6
0003	15 min, ambient	-	30 min, 400°C	-	carbonate wash[b]	0.925	41.5
0004	15 min, ambient	-	60 min, 400°C	-	-	1.06	32.7
0005	15 min, ambient	-	60 min, 400°C	-	water wash	1.04	34.2
0006	15 min, ambient	-	60 min, 400°C	-	carbonate wash	1.01	35.9
0007	15 min, ambient	-	30 min, 500°C	-	-	1.07	32.2
0008	15 min, ambient	-	30 min, 500°C	-	water wash	1.06	32.7
0009	15 min, ambient	-	30 min, 500°C	-	carbonate wash	1.05	32.8
0010	-	carbonate wash[b]	-	-	-	1.50	5.1
0017	15 min, 100°C	-	-	30 min, 600°C	-	0.82	48.4
0018	15 min, 100°C	-	-	30 min, 600°C	water wash	0.76	52.1
0019	15 min, 100°C	-	-	30 min, 600°C	carbonate wash	0.68	57.2
0020	15 min, 100°C	-	-	-	-	-	-
0021	15 min, 100°C	carbonate wash[b]	-	30 min, 600°C	-	0.41	74.1
0022	15 min, 100°C	carbonate wash[b]	-	30 min, 600°C	water wash	0.41	74.1
0023	15 min, 100°C	carbonate wash[b]	-	30 min, 600°C	carbonate wash	0.38	76.0
0024	15 min, 100°C	water wash	-	30 min, 600°C	-	0.72	54.6
0025	15 min, 100°C	water wash	-	30 min, 600°C	water wash	0.72	54.6
0026	15 min, 100°C	water wash	-	30 min, 600°C	carbonate wash	0.71	55.1
0027	15 min, 100°C	carbonate wash	-	30 min, 700°C	-	0.41	74.1
0028	15 min, 100°C	carbonate wash	-	30 min, 700°C	water wash	0.41	74.1
0029	15 min, 100°C	carbonate wash	-	30 min, 700°C	carbonate wash	0.41	74.1

Table 7. Experimental Condition and Results (Continued)

COAL: PSOC 282, Illinois No. 6 (-60 + 100 Tyler Mesh)   Total Sulfur: 1.581 (Wt%)[a]

Experiment No.	Chlorination	Intermediate Wash	Dechlorination with Nitrogen	Advanced Dechlorination with Hydrogen	Post-Treatment	% Total Sulfur in Product[a]	% Desulfurization
0030	-	-	-	30 min, 600°C	-	0.976	38.3
0031	-	-	-	30 min, 600°C	water wash	0.902	42.9
0032	-	-	-	30 min, 600°C	carbonate wash	0.883	44.1
0033	15 min, 100°C	-	-	-	carbonate wash	-	-
0034	15 min, 100°C	carbonate wash	-	30 min, 500°C	-	0.690	56.3
0035	15 min, 100°C	carbonate wash	-	30 min, 500°C	water wash	0.677	57.2
0036	15 min, 100°C	carbonate wash	-	30 min, 500°C	carbonate wash	0.652	58.7
0037	5 min, 100°C	carbonate wash	-	30 min, 700°C	-	0.581	63.2
0038	5 min, 100°C	carbonate wash	-	30 min, 700°C	carbonate wash	0.498	68.5
0039[c]	15 min, 100°C	-	-	30 min, 700°C	-	0.614	61.1
0040[c]	15 min, 100°C	-	-	30 min, 700°C	carbonate wash	0.496	68.6
0041[d]	15 min, 100°C	carbonate wash	-	30 min, 700°C	-	0.517	67.3
0042[d]	15 min, 100°C	carbonate wash	-	30 min, 700°C	carbonate wash	0.517	67.3
0043	15 min, 100°C	carbonate wash	-	10 min, 700°C	-	0.632	60.0
0044	15 min, 100°C	carbonate wash	-	10 min, 700°C	carbonate wash	0.449	71.6
0047	5 min, 100°C	carbonate wash	-	10 min, 700°C	-	0.662	58.1
0048	5 min, 100°C	carbonate wash	-	10 min, 700°C	carbonate wash	0.600	62.0
0049[e]	15 min, 100°C	carbonate wash	-	30 min, 700°C	-	0.521	67.0
0050[e]	15 min, 100°C	carbonate wash	-	30 min, 700°C	carbonate wash	0.409	74.1
0053	15 min, 250°C	carbonate wash	-	30 min, 700°C	-	0 547	65.4
0054	15 min, 250°C	carbonate wash	-	30 min, 700°C	carbonate wash	0.500	68.4

Table 7. Experimental Condition and Results (Continued)

COAL: PSOC 282, Illinois No. 6 (-60 + 100 Tyler Mesh)   Total Sulfur: 1.581 (Wt%)[a]

Experiment No.	Chlorination	Intermediate Wash	Dechlorination with Nitrogen	Advanced Dechlorination with Hydrogen	Post-Treatment	% Total Sulfur in Product[a]	% Desulfurization
0055	15 min, 100°C	-	-	-	-	1.09	29.2
0056[e]	15 min, 100°C	-	30 min, 400°C	-	-	1.076	31.9
0057[e]	15 min, 100°C	-	30 min, 400°C	-	carbonate wash	1.052	33.5
0058[e]	15 min, 100°C	-	30 min, 400°C	30 min, 700°C	-	0.849	46.3
0059[e]	15 min, 100°C	-	30 min, 400°C	30 min, 700°C	carbonate wash	0.850	46.2
0060[e]	15 min, 100°C	carbonate wash	-	30 min, 700°C	-	0.412	73.9
0061[e]	15 min, 100°C	carbonate wash	-	30 min, 700°C	carbonate wash	0.410	74.1
0062[e]	5 min, 100°C	-	-	10 min, 700°C	-	0.990	37.4
0063[e]	5 min, 100°C	-	-	10 min, 700°C	carbonate wash	0.985	37.7

[a]LECO analysis.

[b]Soaked in 10% Na_2CO_3 solution for 30 min, followed by washing with distilled water until free of alkali, then dried

[c]Coal initially washed with 10% Na_2CO_3 solution and dried.

[d]Chlorination with a 4:1 mixture of nitrogen and chlorine.

[e]-100 + 200 Tyler Mesh.

96

Table 8. Experimental Condition and Results

COAL: PSOC 276, Ohio No. 8 (-60 + 100 Tyler Mesh)   Total Sulfur: 3.75 (Wt%)[a]

Experiment No.	Chlorination	Intermediate Wash	Dechlorination with Nitrogen	Advanced Dechlorination with Hydrogen	Post-Treatment	% Total Sulfur in Product[a]	% Desulfurization
0011	15 min, 100°C	-	30 min, 400°C	30 min, 600°C	-	2.60	30.6
0012	15 min, 100°C	-	30 min, 400°C	30 min, 600°C	water wash	2.33	37.9
0013	15 min, 100°C	-	30 min, 400°C	30 min, 600°C	carbonate wash[b]	2.23	40.5
0045	15 min, 100°C	carbonate wash[b]	-	30 min, 700°C	-	0.708	81.1
0046	15 min, 100°C	carbonate wash[b]	-	30 min, 700°C	carbonate wash	0.699	81.3
0051[c]	15 min, 100°C	carbonate wash	-	30 min, 700°C	-	1.113	70.3
0052[c]	15 min, 100°C	carbonate wash	-	30 min, 700°C	carbonate wash	0.943	74.9
0064	5 min, 100°C	-	-	-	-	2.81	27.4
0065	30 min, 100°C	-	30 min, 600°C	30 min, 700°C	-	2.11	43.7
0066	30 min, 100°C	-	30 min, 600°C	30 min, 700°C	carbonate wash	1.67	55.5
0067	5 min, 100°C	-	10 min, 600°C	10 min, 700°C	-	2.750	26.7
0068	5 min, 100°C	-	10 min, 600°C	10 min, 700°C	carbonate wash	1.870	50.1
0069	5 min, 100°C	carbonate wash	10 min, 600°C	10 min, 700°C	-	1.47	60.8
0070	5 min, 100°C	carbonate wash	10 min, 600°C	10 min, 700°C	carbonate wash	1.46	60.9

[a]LECO analysis.

[b]Soaked in 10% Na_2CO_3 solution for 30 min followed by washing with distilled water until free of alkalai, then dried.

[c]-100 + 200 Tyler Mesh.
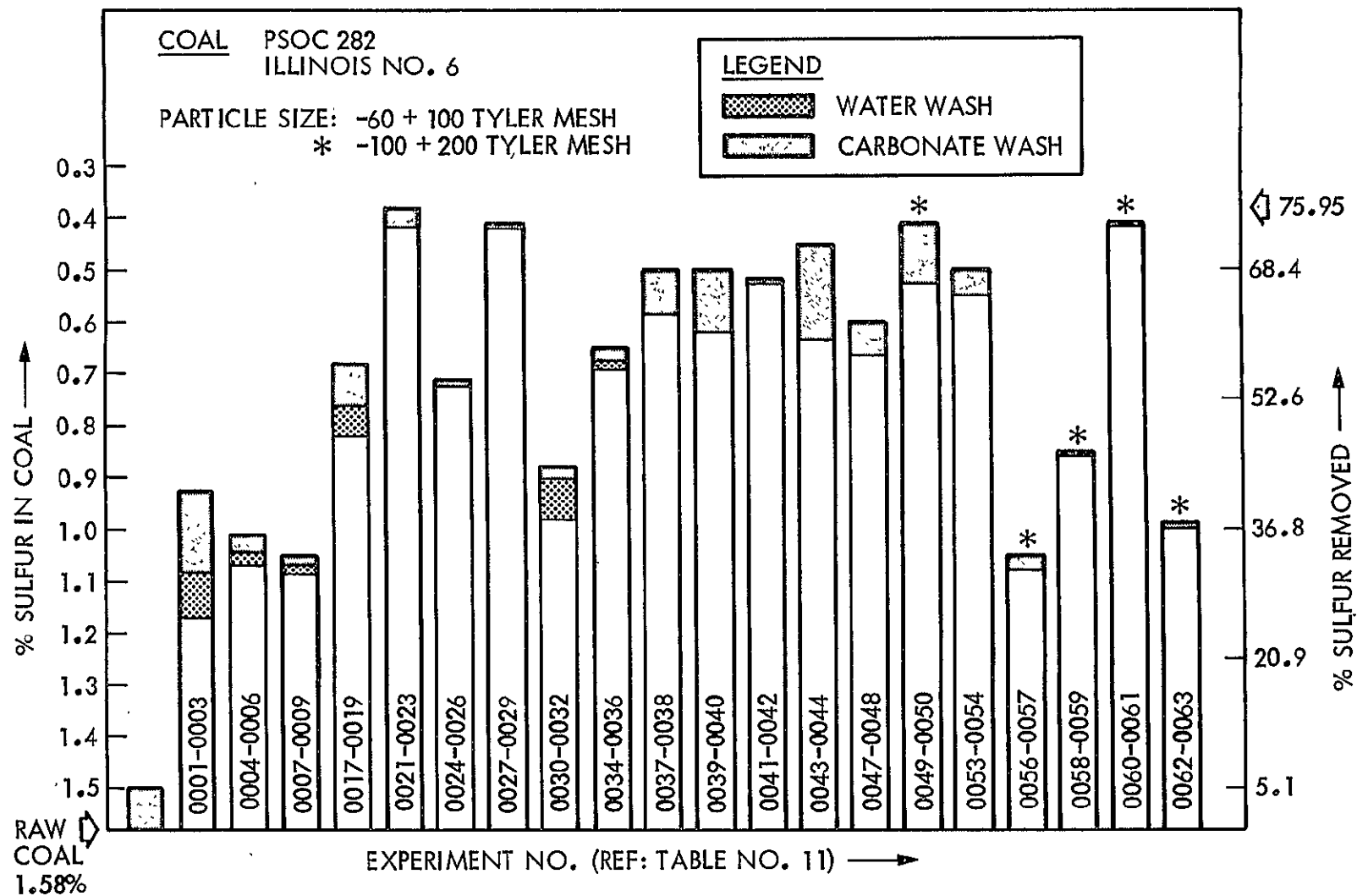
Figure 19. Experimental Results of Fluidized Bed Coal Desulfurization, PSOC 282, Illinois No. 6
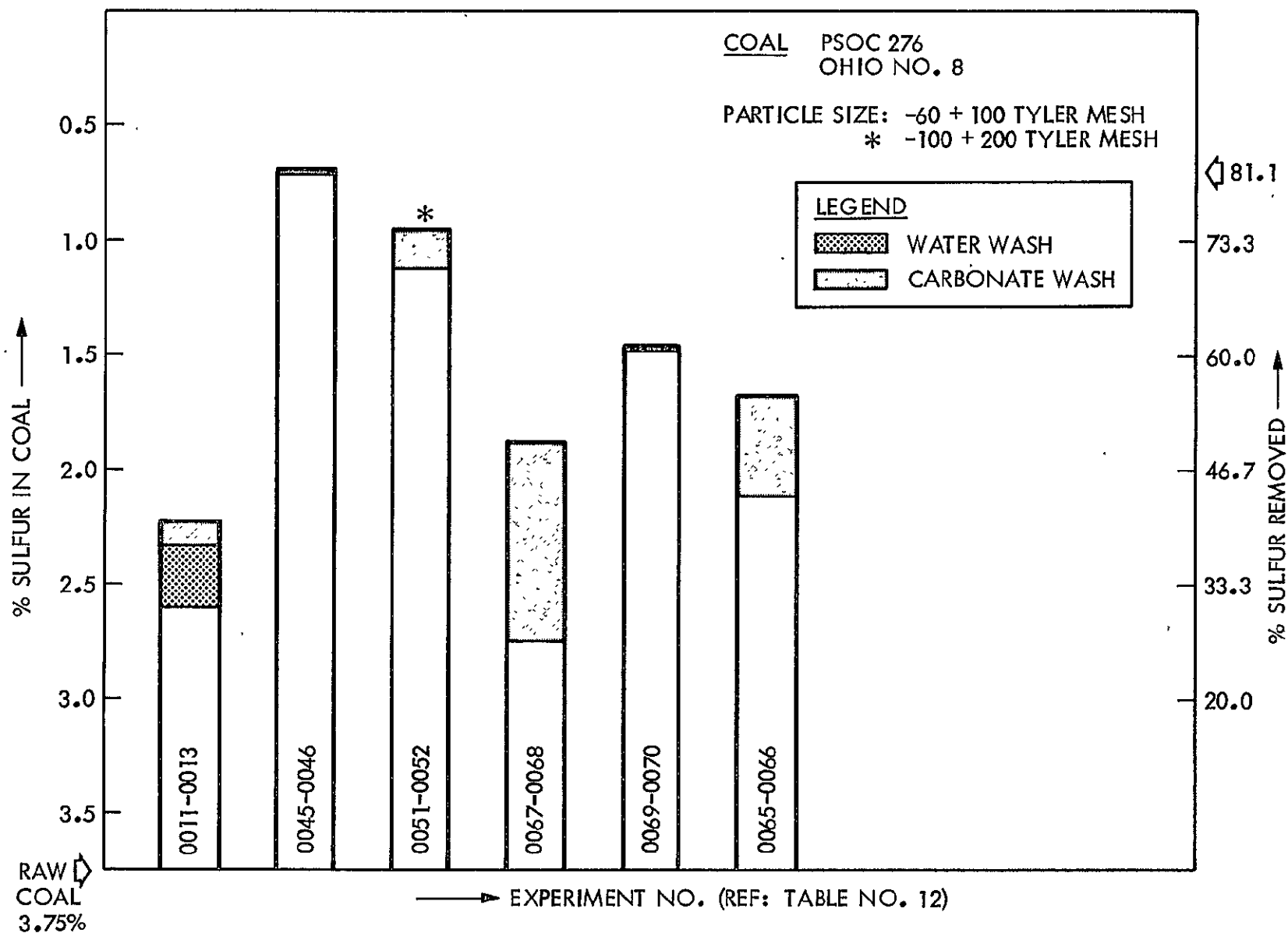
Figure 20. Experimental Results of Fluidized Bed Coal Desulfurization, PSOC 276, Ohio No. 8

1. Chlorination

    Chlorination in general was carried out at about 100°C for 15 min.
    In certain cases chlorination for as short a time interval as 5 min
    (Runs 0037, 0047, 0062) as well as at 250°C (Run 0053) was also
    carried out. The effect of changing chlorine concentration by
    employing a 4:1 mixture of nitrogen to chlorine (Run 0041) was also
    studied. However, due to the high levels of chlorine that are
    likely to exist in chlorinated coals prior to dechlorination, sul-
    fur estimation in chlorinated coals could not be carried out due to
    interferences in the LECO method. Consequently, these results are
    discussed based on sulfur estimations of the product coals in sub-
    sequent sections on dechlorination and hydrodesulfurization in this
    document.

2. Dechlorination

    Dechlorination of chlorinated coals by nitrogen was carried out at
    400 to 600°C for 30 min. In general, dechlorination at higher
    temperatures did not result in any significant change in the desul-
    furization levels achieved. However, longer times and higher
    temperatures during dechlorination were effective to a limited
    extent in reducing the chlorine levels in product coals.

3. Hydrodesulfurization

    Substitution of hydrogen during dechlorination was found to further
    enhance the desulfurization levels achieved. In fact,
    dechlorination-cum-hydrodesulfurization by hydrogen was found to be
    superior to dechlorination by nitrogen alone or successive
    dechlorination and hydrodesulfurization. Hydrodesulfurization was
    carried out at atmospheric pressure for 10 to 30 min at 500 to
    700°C.

    Hydrodesulfurization of chlorinated coal at 600°C resulted in
    increasing the level of desulfurization to 48% (Run 0017) compared
    to the 30% during dechlorination. While the increase in the level
    of desulfurization is not significant, raw coal itself was desul-
    furized to the extent of 38% at 600°C, the reduction in the
    chlorine level was substantial.

    Treatment for coal prior to hydrodesulfurization as well as hydro-
    desulfurized coals resulted in a marked increase in the desulfur-
    ization levels achieved as indicated by the results presented in
    Table 7. A carbonate wash to the chlorinated coals prior to hydro-
    desulfurization was more effective than a water wash. An inter-
    mediate carbonate wash increased the level of desulfurization to
    74% (Run 0021) compared to 48% achieved with no wash at all (Run
    0017), while a simple water wash resulted in only 55% desulfur-
    ization. The data presented in Table 7 also indicate that a sub-
    sequent wash to hydrodesulfurized coals that were treated with

carbonate prior to hydrodesulfurization did not significantly enhance the level of desulfurization. The substantial reduction in sulfur levels in coals as a consequence of carbonate treatment to chlorinated coals is likely, due to the removal of organic sulfur by alkali. Alkali treatment of coal results in the removal of both pyritic and organic forms of sulfur, more so if the coal is initially subjected to an oxidation treatment. The minor reductions in sulfur levels achieved by subjecting product coals to a carbonate wash may be the result of trapping sulfur in the ash during combustion by sodium ions that might have been retained in the coal. It is believed that alkaline metals such as sodium, calcium, etc. either chemically bound to coal or in a physical mixture with coal are capable of reducing potential sulfur emissions during coal combustion by trapping the sulfur in the ash as sulfate.

Treating raw coal with carbonate solution prior to desulfurization resulted in achieving a desulfurization level of 61% (Run 0039).

Because gaseous chlorine was employed as the fluidizing medium, chlorine requirement in the process could be reduced by either reducing the time of reaction or by reducing the chlorine concentration in the feed by diluting it with an inert gas. Both these alternatives were found to result in high levels of desulfurization. By chlorinating for only 5 min (Run 0037) as much as 63% desulfurization was achieved, while a mixture of 4:1 nitrogen and chlorine during chlorination (Run 0039) resulted in 61% desulfurization.

Even the time of hydrodesulfurization can be reduced without sacrificing the level of desulfurization, as indicated by Run 0043 in which 60% desulfurization was achieved. Reduction of the time of chlorination and hydrodesulfurization by as much as one-third (Run 0047) resulted in 58% desulfurization. The data clearly shows that shorter reaction times and lower reactant concentrations can be used while still achieving higher levels of desulfurization. However, a more detailed parametric study is needed to establish optimum conditions of operation.

Higher temperature during chlorination did not result in any significant enhancement of the level of desulfurization as indicated by Run 0053 in which 250°C during chlorination resulted in only 65% desulfurization.

Particle size also did not have a significant effect within the range of particle sizes studied. (Compare Runs 0027 and 0060 for -60 +100 mesh and -100 +200 mesh, respectively.)

B. PSOC 276 Coal

A limited number of experiments was conducted employing PSOC 276 coal. The maximum level of desulfurization achieved was once again 81% (Run 0045). The general trend was the same as with PSOC 282 coal in that:

(1) Substitution of hydrogen during dechlorination markedly improved the level of desulfurization.

(2) Particle size did not have any effect in the range of sizes studied.

(3) Even 5 min of chlorination and 10 min of dechlorination cum-hydrodesulfurization resulted in 60% desulfurization.

(4) Carbonate wash prior to hydrodesulfurization significantly enhanced the level of desulfurization.

(5) Longer times of chlorination and dechlorination did not enhance desulfurization.

IX. SCANNING ELECTRON MICROSCOPY (SEM) EXAMINATION OF COAL SURFACE

During desulfurization treatments coal undergoes various chemical changes which will also be reflected in changes in the gross physical structure. One convenient method of assessing the physical changes undergone by coal surface is Scanning Electron Microscopy (SEM). Due to the imaging process inherent with SEM, coal particles can be examined at magnifications up to 10,000 times while maintaining a sufficiently large depth of field to render a three-dimensional quality to the image. However, the technique is limited to an examination of the exterior surface of the particles and precludes any quantitative measurements. Even so, such information should provide a good qualitative indication of the changes undergone by the particle interior.

By using SEM along with EDAX (Energy Dispersive Analyzer for X-Rays), it is possible to obtain a relative comparison of the levels of sulfur and mineral components in coal. While this information is qualitative, it nevertheless provides a basis for quickly comparing the levels of common mineral components and sulfur in coal and the effect of different treatments to coal.

A. SEM PHOTOGRAPHS

PSOC 276 and PSOC 282 raw coals as well as product coals from some typical experiments were examined by SEM (see representative photographs at 100 and 10,000 magnification in Figures 7 through 14).

Figures 7 and 13 show the SEM photographs of PSOC 282 and PSOC 276 coals, respectively. Both photographs show the same general features. The coal particles are covered and interspaced by several smaller particles, which appear to adhere to the larger particles. The dimensions of the coal particles range from 50 to 200 μm while a majority of the small particles are of the order of 1 μm or smaller. It is possible that the small particles are formed during the process of grinding and are not removed during sieving.

Washing PSOC 282 raw coal with 1 M Na_2CO_3 solution appears to have removed a majority of the small particles from the coal surface. As the reduction in sulfur by the carbonate wash is only about 5%, it is reasonable to assume that the smaller particles may essentially consist of mineral matter besides pyrites.

Figures 9 through 12 and Figure 14 present the SEM photographs of desulfurized coals. These photographs in general show that the desulfurization treatments resulted in a substantial cleaning of the coal surface not achieved by a carbonate wash. They also show that, not only are the coal surfaces clean, but they also appear to be etched. Some of the particles also appear to have developed fissures. While the raw coal particle surfaces are smooth, the product coal particle surfaces appear to be rough with noticeable cracks. These features are indicative of the removal of some portions from the coal surface as well as a breakdown of structure in some cases during the desulfurization treatments.

53

B. EDAX SPECTRA

EDAX Spectra (Energy Dispersive Analyzer for X-Rays) of PSOC 282 and PSOC 276 raw coals as well as some desulfurized coals are presented in Figures 15 through 18. The EDAX spectrum of PSOC 282 raw coal (1.581 wt% total sulfur) presented in Figure 15 indicates that the peak corresponding to sulfur is much smaller compared to the one for PSOC 276 raw coal shown in Figure 18, which contains over twice the amount of sulfur (3.75 wt% total sulfur). Comparison of the spectra of carbonate washed PSOC 282 coal shown in Figure 15 with that of the raw coal reveals that the wash has resulted in the reduction of sulfur and mineral matter, which supports the conclusion from the SEM photographs. EDAX spectra of desulfurized coals from experiments 0023 (76% sulfur removal) and 0027 (74% sulfur removal) presented in Figures 16 and 17 show smaller sulfur peaks compared to the raw coal. The same trend was observed from the EDAX spectrum of PSOC 276 desulfurized coal from experiment 0046 (80% sulfur removal) presented in Figure 18. In spite of the different conditions of treatments, the EDAX spectra of desulfurized coals did not show any significant increase in the levels of chlorine and sodium retained in the coals after the treatment. The increase in iron peak observed in some of the samples was unexpected.

C. CONCLUSIONS

SEM photographs of raw and desulfurized coals show that desulfurization treatments result in changes in the gross physical structure of coal. After treatments, coal surfaces not only appeared to be clean but also developed cracks and rough surfaces indicative of a breakdown of physical structure and loss of material from the surface.

The EDAX spectra show that sulfur peaks in the desulfurized coals are reduced when compared to raw coals. Apart from some reductions in the Al and Si levels in the desulfurized coals, the treatments did not result in any significant enhancement in either chlorine or sodium retained in the product coal.

X. RESULTS OF CSMRI ANALYSES

A. TOTAL SULFUR AND SULFUR FORMS

Ten coal samples from typical experiments were analyzed at the Colorado School of Mines Research Institute (CSMRI) for total sulfur and sulfur forms by ASTM-approved methods. In general, the total sulfur estimations by LECO acid-base analysis were in agreement with the CSMRI values. Some anomalies were observed in the CSMRI results on sulfur forms such as an increase in organic sulfur fraction in coal after desulfurization in spite of substantial reductions in total sulfur, pyritic sulfur and sulfate sulfur. This anomaly is more likely to be due to the analytical bias rather than by any transformation of pyritic sulfur to organic form. In view of the fact that organic sulfur is calculated by difference, any errors in estimating total iron and pyritic iron could lead to such anomalies. Therefore, more precise methods for characterizing sulfur distribution in coal as well as for the direct estimation of organic sulfur are needed.

1. PSOC 282 Coal

Samples from six typical experiments were analyzed for total sulfur and sulfur forms at CSMRI. The results are presented in Table 9. Pyritic sulfur reductions were uniformly above 90% except in the case where the coal was only chlorinated (48%). Sulfate sulfur reductions were also high. Organic sulfur reductions varied from 21 to 34% except in two cases where there was an apparent increase. In samples from experiments 0017 and 0039 (where the coals were not subjected to any post or intermediate washing treatments) the pyritic sulfur was reduced by 90%. Thus it appears that the sulfur is removed as gas-phase species and lends support to the proposed mechanism. This is also evident from the results of experiment 0055 in which coal was only chlorinated, resulting in 49% pyritic sulfur reduction. Consequently, in the proposed process an intermediate wash between chlorination and dechlorination and/or hydrodesulfurization steps appears to be totally unnecessary, thereby simplifying the process considerably.

2. PSOC 276 Coal

Four samples from typical experiments were analyzed at CSMRI for total sulfur and sulfur forms. The results are presented in Table 10. Again, there was some analytical bias in organic sulfur estimations.

In experiment 0045, in which maximum desulfurization of 82% was achieved, the reductions in pyritic, sulfate and organic sulfur were 99, 100 and 43%, respectively.

Table 9.   Total Sulfur and Forms of Sulfur in
Selected Product Coals[a], PSOC 282

Sample No.	Experiment[b] No.	Total Sulfur[c]		Pyritic Sulfur[c]		Sulfate Sulfur[c]		Organic Sulfur[c,d]	
		wt%	% Removed	wt%	% Removed	wt%	% Removed	wt%	% Removed
-	Raw Coal	1.54	-	0.43	-	0.36	-	0.75	-
1	0017	0.84	45.4	0.04	90.8	<0.05	86.1	0.80	+6.7
2	0039[e]	0.63	59.1	0.04	90.7	<0.05	86.1	0.59	21.3
3	0041[f]	0.58	62.3	0.03	93.0	<0.05	86.1	0.55	26.7
5	0055[g]	1.09	29.2	0.22	48.8	0.29	19.5	0.58	22.7
6	0058	0.81	47.4	0.03	93.0	<0.05	86.1	0.78	+4.0
7	0060	0.51	66.9	0.02	95.4	<0.05	86.1	0.49	34.7

[a]Analyses carried out at CSMRI.

[b]For experimental details refer to Table 7.

[c]As determined basis.

[d]By difference.

[e]Coal pretreated with 1 M Na_2CO_3 solution.

[f]Mixture of N_2/Cl_2 (4:1) during chlorination.

[g]Chlorination only.

Table 10. Total Sulfur and Forms of Sulfur in
Selected Product Coals[a], PSOC 276

Sample No.	Experiment[b] No.	Total Sulfur[c]		Pyritic Sulfur[c]		Sulfate Sulfur[c]		Organic Sulfur[c,d]	
		wt%	% Removed	wt%	% Removed	wt%	% Removed	wt%	% Removed
-	Raw Coal	3.87	-	2.63	-	0.06	-	1.17	-
4	0045	0.70	81.9	0.03	98.8	<0.05	-	0.67	42.7
8	0064[e]	2.81	27.4	0.72	72.6	1.02[g]	-	1.07	8.5
9	0067	2.29	40.8	0.13	95.0	<0.05	-	2.16[g]	-
10	0069[f]	1.73	55.3	0.04	98.5	<0.05	-	1.69[g]	-

[a]Analyses carried out at CSMRI.

[b]For experimental details refer to Table 8.

[c]As determined basis.

[d]By difference.

[e]Chlorination only.

[f]5 min chlorination and 10 min dechlorination and hydrodesulfurization.

[g]Anamolous results showing a substantial increase.

In experiments 0064, 0067 and 0069 the coal was chlorinated for 5 min and dechlorinated/hydrodesulfurized for 10 min. Chlorination alone for as short a time as 5 min removes as high as 73% of the pyritic sulfur. Results of these experiments in which coals were not subjected to any washing treatment lend support to the contention that the sulfur is removed in the gas-phase and no intermediate washing step is necessary.

PSOC 276 coal is desulfurized to a greater extent compared to PSOC 282 coal. Even 5 min chlorination followed by 10 min of dechlorination has resulted in 99% reduction in pyritic sulfur.

3. Comparison of CSMRI and LECO Analyses

Table 11 presents the results of CSMRI and LECO analyses for total sulfur in the present investigation. The values are in agreement with an average deviation of 8.8%.

B. PROXIMATE AND ULTIMATE ANALYSES

Four samples of chlorinated coals and chlorinated and desulfurized coals were analyzed at CSMRI for long proximate and ultimate analyses. The results are presented in Table 12.

.1. PSOC 282 COAL

Proximate and ultimate analyses of raw coal, coal chlorinated at 100C for 15 min and chlorinated coal hydrodesulfurized at 700C for 30 min are presented in Table 12.

By chlorination only the ash, carbon, hydrogen, sulfur and nitrogen contents slightly decreased while the oxygen content remained unchanged. There was a significant drop in heating value and substantial increase in chlorine content (12.9% compared to 0.47% in raw coal).

Dechlorination-cum-hydrodesulfurization resulted in a slight increase in the ash content and heating values. The volatiles decreased considerably (from 33.8% in raw coal to 5.9%), fixed carbon value increased substantially (87.2% compared to 59.5% in raw coal), carbon content increased from 74.8% to 85.8%, hydrogen content decreased from 4.8% to 2%, and nitrogen content remained almost unchanged. Hydrogen treatment resulted in a substantial decrease in the sulfur content (1.6% to 0.49%) and oxygen content (10% to 2.63%). The chlorine content after the dechlorination-cum-hydrodesulfurization treatment was almost the same as in the raw coal.

Table 11. Comparison of Total Sulfur Estimation
by Eschka and LECO Methods

Sample No.	Experiment No.[a]	Eschka Analysis[b]	LECO Analysis[c]	Difference Eschka-LECO	% Deviation
PSOC 282 COAL (Illinois No. 6)
-	Raw Coal	1.54	1.58	-0.04	-2.5
1	0017	0.84	0.82	+0.02	+2.4
2	0039	0.63	0.61	+0.02	+3.3
3	0041	0.58	0.52	+0.06	+11.5
5	0055	1.09	-	-	-
6	0058	0.81	0.85	-0.04	-4.7
7	0060	0.51	0.41	+0.10	+24.4
PSOC 276 COAL (Ohio No. 8)
-	Raw Coal	3.87	3.75	+0.12	+3.2
4	0045	0.70	0.71	-0.01	-1.4
8	0064	2.81	-	-	-
9	0067	2.29	2.75	-0.46	-16.7
10	0069	1.73	1.47	+0.26	+17.6

PERCENT AVERAGE DEVIATION: 8.8

[a]For experimental details refer to Tables 7 and 8.
[b]Analyses carried out at CSMRI.
[c]Analyses carried out at JPL.

Table 12. Proximate and Ultimate Analyses of Selected Product Coals[a]

Coal	Sample No.	Experiment No.[b]	Moisture[c] %	Ash, %		Volatile Matter, %		Fixed Carbon, %		Heating Value, Btu/lb		Carbon, %	
				AD[c]	Dry[d]	AD	Dry	AD	Dry	AD	Dry	AD	Dry
PSOC 282	0	Raw Coal[f]	3.1	-	6.70	-	33.80	-	59.50	-	13,092	-	74.8
PSOC 282	A	0055	3.61	5.88	6.10	34.50	35.80	56.00	58.10	10,752	11,150	62.40	62.70
PSOC 282	B	0060	2.13	6.78	6.93	5 77	5.90	85.30	87.20	13,372	13,666	84.00	85.80
PSOC 276	0	Raw Coal[f]	1.89	-	11.50	-	37.20	-	51.30	-	12,755	-	71.60
PSOC 276	C	0064	2.73	10.40	10.70	35.30	36.30	51.60	53.00	11,165	11,478	63.60	65.40
PSOC 276	D	0069	1.31	12.80	13.00	7.09	7.18	78.80	79.80	12,580	12,744	79.10	80.10

Sample No.	Hydrogen, %		Sulfur, %		Nitrogen, %		Chlorine, %		Oxygen, %[e]	
	AD	Dry	AD	Dry	AD	Dry	AD	Dry	AD	Dry
0	-	4.82	-	1.60	-	1.69	-	0.47	-	10.00
A	4.22	3.96	1.16	1.20	1.27	1.32	12.40	12.90	12.70	9.82
B	2.20	2.00	0.48	0.49	1.60	1.64	0.50	0.51	4.44	2.63
0	-	5.67	-	3.91	-	1.28	-	0.16	-	5.87
C	4.70	4.52	2.84	2.92	1.11	1.14	4.43	4.55	12.90	10.80
D	2.21	2.09	1.63	1.65	1.38	1.40	0.13	0.13	2.75	1.63

[a] Analysis carried out at CSMRI.

[b] For experimental details refer to Tables 7 and 8.

[c] As determined basis.

[d] Dry basis.

[e] By difference.

[f] From Phase III Report (Ref. 3).

As a result of the desulfurization process there is a net increase in the ash content and heating values, a substantial increase in fixed carbon and carbon values, and a significant decrease in the volatile matter, hydrogen, sulfur and oxygen contents. Nitrogen and chlorine values remained essentially unchanged.

2. PSOC 276 COAL

Proximate and ultimate analyses of PSOC 276 raw coal, coal chlorinated at 100°C for 5 min and chlorinated coal dechlorinated at 600°C for 10 min and hydrodesulfurized at 700°C for 10 min are presented in Table 12.

As a consequence of chlorination there was an initial decrease in ash content, heating value, carbon, and nitrogen. The chlorine content increased substantially (from 0.16 to 4.55%). After dechlorination and hydrodesulfurization there was a net increase in the ash content (11.5 to 13.0%), fixed carbon (51.3 to 78.8%), carbon (71.6 to 80.1%) and nitrogen (1.28 to 1.4%). The increase in nitrogen content in this case may be due to successive dechlorination and hydrodesulfurization instead of dechlorination-cum-hydrodesulfurization as in the case of PSOC 282 coal. The volatile matter decreased from 37.2 to 7.2%, hydrogen decreased from 5.67 to 2.1%, sulfur decreased from 3.91% to 1.63% and oxygen decreased from 5.87 to 1.63%. The heating value and chlorine content remained unchanged. In fact, the chlorine content of the desulfurized coal is even slightly lower than the raw coal.

In general, the desulfurization treatments resulted in a slight net increase in ash content and heating value, a substantial increase in fixed carbon and carbon values, and an equally substantial reduction in volatile matter, hydrogen, sulfur and oxygen contents.

CONCLUSIONS

Proximate and ultimate analyses of raw, chlorinated and dechlorinated and/or hydrodesulfurized coals revealed that the desulfurization process results in product coals with increased fixed carbon and carbon contents and substantially reduced volatiles, hydrogen, and oxygen contents. There was a net increase in ash content and heating values.

The nitrogen and chlorine contents remained essentially unchanged.

The results show that further reductions are possible in chlorine requirement in the process and that the use of chlorine in the process has not resulted in any increased chlorine levels in the product coals. This is significant because of environmental implications and corrosion considerations. The results also indicate that an intermediate wash to chlorinated coals may be totally unnecessary, thereby making the process simpler and more economical than present processes.

61

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APPENDIX A

Operating Procedure for the Laboratory Scale Batch Fluidized
Bed Reactor System for Coal Desulfurization

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OPERATING PROCEDURE FOR THE LABORATORY SCALE BATCH
FLUIDIZED BED REACTOR SYSTEM FOR COAL DESULFURIZATION

INTRODUCTION

is standard operating procedure outlines the conditions required for the
fe operation of the laboratory scale batch fluidized bed reactor system for
al desulfurization shown in Figure 1.

. OPERATING RULES AND CONDITIONS

eration of the batch fluidized bed reactor system is subject to specific
les and conditions. Prior to beginning an experimental run, the following
eps must be completed:

(1) The reactor and accessories must be connected in the sequence shown
in Figure 1.

(2) The entire system must be leakproof.

(3) A complete description of an experimental run must be made
available to the operator.

(4) Excess chlorine gas during chlorination must be scrubbed with
sodium carbonate solution.

(5) Hydrochloric acid gas and hydrogen sulfide gas generated during
dechlorination and hydrodesulfurization, respectively, must be
scrubbed with sodium carbonate solution.

I. PERSONNEL SAFETY

rsonnel operating the batch-fluidized bed reactor system should be equipped
th:

(1) Protective garments, such as a laboratory coat and rubber or
asbestos gloves.

(2) Protective eye glasses.

(3) Proper respiratory equipment, such as gas masks for toxic gases and
coal dust.

(4) Fire extinguishing equipment in proper working condition and a
water shower.

IV. EQUIPMENT SAFETY

To ensure safe conditions, specific precautions with equipment must be taken.

A. CHLORINATION

(1) Do not allow liquid chlorine into the reactor. A mixture of liquid chlorine and coal is potentially explosive.

(2) Preheat the chlorine to ensure that it is vaporized.

(3) If leaks develop during a run, repair them immediately; otherwise, stop the chlorine flow and abort the run.

(4) Ensure that the exhaust in the fuming cupboard is working at all times during an experiment.

(5) At the end of prescribed reaction time shut off the chlorine flow. Purge the system with nitrogen.

(6) Make certain that the coal is being fluidized by observing the minor pressure drop fluctuations in the manometer.

(7) The reactor should be adequately insulated to conserve the heat generated during chlorination.

(8) Ensure that the scrubber is working satisfactorily.

B. DECHLORINATION

(1) The batch-fluidized bed dechlorinator system should be operated in an oxygen-free environment to avoid possible coal combustion and explosion.

(2) The reactor should be properly insulated to reduce radiation losses.

(3) Hydrochloric acid vapors should be scrubbed with sodium carbonate solution.

(4) Check periodically that the heater controller is working properly.

(5) Maintain the nitrogen flow through the reactor at all times during dechlorination and cooling. Failure to do so may cause fire and/or an explosion.

(6) In case of fire, shut off the heaters and smother the fire with a nitrogen flow and/or a CO_2 fire extinguisher.

C. HYDRODESULFURIZATION

Before hydrogen is fed into the reactor, the following tasks must be completed:

(1) The hydrogen cylinder, control valves and pressure gage must be installed outside the building, away from the reactor system.

(2) The reactor system should be completely leakproof. Check it by feeding nitrogen under slight pressure.

(3) The reactor should be adequately insulated with no heater parts exposed.

(4) The operator should close the door of the fuming cupboard containing the reactor system and stay away from the reactor system.

(5) Heat the reactor to the required temperature under nitrogen blanket before feeding hydrogen.

(6) After the hydrodesulfurization experiment is completed, shut off the hydrogen supply and switch off the heaters simultaneously; then cool the reactor under nitrogen atmosphere.

(7) In case of fire during hydrodesulfurization, stop feeding hydrogen immediately, start nitrogen flow to the reactor, wait for 2 or 3 minutes in order to purge the system and put the fire out.

(8) Check that the exhaust in the fuming cupboard is working at all times during hydrodesulfurization.

D. REACTOR AND ACCESSORIES

(1) Before starting a run, ensure that the reactor and accessories are thoroughly cleaned after the previous experiment and are connected in sequence.

(2) Load the reactor with coal, position securely in place and make the appropriate connections to the accessories such as manometer, condenser, etc.

(3) Mount the heaters on the reactor and lag them properly before making the power connections.

(4) Fill the scrubber with 1 M Na_2CO_3 solution.

(5) Ensure that the exhaust fan is working.

(6) Always start a run by feeding nitrogen into the reactor first and ensuring that the system is free of oxygen.

(7) After a run, clean the entire system thoroughly in preparation for the next experiment.

V. OPERATING PROCEDURE

The following standard operating procedure should be available to the operator prior to starting an experiment.

A. START-UP

(1) Weigh the required quantity of dry coal (dried in an oven at 100°C for 6 hours and cooled in a desiccator) and transfer it to the reactor.

(2) Position the reactor in place and connect the accessories.

(3) Connect the pressure drop tappings to the manometer.

(4) Fill the scrubber with 1 M Na_2CO_3 solution and connect it to the system.

(5) Start water flow through the glass condenser.

(6) Mount the reactor heaters, insulate them and make the appropriate connections to the controller and power supply.

(7) Switch on the exhaust in the fuming cupboard.

(8) Check the system for leaks by feeding nitrogen under slight pressure.

(9) Adjust the flow of nitrogen so that the bed is fluidized as indicated by the manometer reading.

(10) Switch on the power supply to the preheater and reactor heaters, set the temperature control for the required temperature and allow the system to reach stable condition.

B. CHLORINATION

(1) After the reactor has attained the set temperature, start chlorination by stopping the nitrogen flow and feeding chlorine at the required flow rate. Ensure that the bed is properly fluidized by tapping the reactor if necessary. (During the first few minutes of chlorination, coal has a tendency to consolidate due to the heat generated.)

(2) Conduct the run for the required time interval.

(3) After chlorination, stop chlorine flow and start feeding nitrogen at the required flow rate.

C. DECHLORINATION

(1) Set the reactor temperature to the required level.

(2) After the required temperature is attained, conduct dechlorination for the required time interval.

D. HYDRODESULFURIZATION

(1) Set the reactor temperature to the desired level and allow the reactor to attain the temperature.

(2) After the reactor has attained the temperature, start hydrodesulfurization by shutting off the nitrogen flow and feeding hydrogen at the flow rate required for fluidization.

(3) Conduct the run for the required time interval.

(4) After hydrodesulfurization, stop the hydrogen flow, begin feeding nitrogen and switch off the power supply to the preheater and reactor heaters.

(5) In case of dechlorination-cum-hydrodesulfurization, omit Step C (Dechlorination) and continue with Step D after Step B (Chlorination).

E. SHUT-DOWN

(1) Allow the reactor to cool to the ambient temperature in a nitrogen blanket.

(2) Stop nitrogen flow, dismantle the heaters from the reactor, and disconnect the reactor from the manometer and the rest of the assembly.

(3) Collect and weigh the product coal from the reactor.

(4) Collect the condensate from the receiver.

(5) Collect a sample of the scrubber solution.

(6) Clean the reactor and accessories thoroughly.

APPENDIX B

Procedure to Determine Sulfur Forms in Coal
(ASTM Method)

ANALYTICAL PROCEDURE TO DETERMINE SULFUR FORMS IN COAL (ASTM METHOD)

A. SUMMARY OF THE METHOD

(1) Sulfate sulfur is determined by extracting a weighed sample of coal with dilute hydrochloric acid followed by precipitation with barium chloride ($BaCl_2$) and weighing the precipitate as barium sulfate ($BaSO_4$). Sulfate sulfur is soluble in diluted hydrochloric acid while pyritic and organic forms of sulfur are not.

(2) Pyritic sulfur is determined by extracting a weighed sample of coal with dilute nitric acid followed by titrimetric or atomic absorption determination of iron in the extract as a measure of pyritic sulfur. Extraction of pyritic sulfur from coal with dilute nitric acid involves the oxidation of ferrous iron to ferric iron and sulfide sulfur to sulfate sulfur, both of which are soluble in nitric acid. Since a small amount of organic sulfur is also dissolved along with sulfate and pyritic sulfur during extraction, the dissolved sulfur is not a reliable measure of pyritic sulfur. Consequently, it is estimated by determining the amount of iron present in the pyrite, which is obtained from the difference between nitric acid and hydrochloric acid soluble iron. However, there are certain limitations to the use of sulfate sulfur residue for the determination of pyritic sulfur in coal. For example, if pyritic iron is high, then the large sample required for determining the small amounts of sulfate sulfur will contain large quantities of iron and may require dilution. In addition, the determination of pyritic iron cannot be carried out until both extractions for sulfur have been completed.

(3) Organic sulfur is determined by subtracting the sum of sulfate sulfur and pyritic sulfur from the total sulfur as determined by the Eschka Method (ASTM Method D-3177).

B. REAGENTS

(1) Barium chloride solution (100 g/l) - Dissolve 100 g of barium chloride ($BaCl_2 \cdot 2H_2O$) in water and dilute to 1000 ml.

(2) Hydrochloric acid (2 + 3) - Mix 2 volumes of concentrated hydrochloric acid (specific gravity 1.19) with 3 volumes of water.

(3) Hydrochloric acid (1 + 23) - Mix 1 volume of concentrated hydrochloric acid (specific gravity 1.19) with 23 volumes of water.

(4) Nitric acid (1 + 7) - Mix 1 volume of concentrated nitric acid (specific gravity 1.42) with 7 volumes of water.

C. PROCEDURE

1. Sulfate Sulfur

a. **Extraction of sulfate sulfur.** Weigh to the nearest 0.1 mg about 5 g of thoroughly mixed air-dried coal that has been ground to pass a No. 60 sieve, transfer to a 250-ml Erlenmeyer flask, and add 50 ml of HCl (2 + 3). Fit the cold-finger condenser into the neck of the flask, place on a hot plate and boil for 30 min. Rinse the cold-finger condenser into a flask with HCl (1 + 23) and filter through a medium textured double acid-washed filter paper into a 400-ml beaker. Transfer the residue to the filter, wash six times with HCl (1 + 23) using a total of about 35 ml and determine sulfate sulfur in the filtrate as decribed in (b) and (c) below. The residual coal may be retained for the determination of pyritic sulfur. Discard the residual coal if separate sample is used for the pyritic sulfur determination.

b. **Removal of iron.** To the filtrate obtained from (a) above, add 10 ml of saturated bromine water, cover with a watch glass, and boil for 5 min to ensure that all iron is in the ferric state. Expell excess bromine. Precipitate iron by slowly adding NH_4OH (specific gravity 0.90) until a slight excess is present, then add 5 ml more, while stirring to coagulate the yellowish brown ferric hydroxide precipitate. Place the covered beaker on a hot plate and boil for 1 min. Filter the iron precipitate using an ashless, medium-texture filter paper and collect the filtrate in a 600-ml beaker. Wash the precipitate several times with hot water to which a trace of NH_4OH and NH_4Cl has been added. Retain the filtrate with washings for the determination of sulfur and the precipitate with the original beaker for the determination of non-pyritic iron.

c. **Final determination of sulfate sulfur.** Neutralize the filtrate from (b) above with concentrated HCl (specific gravity 1.19) and add an excess of about 1 ml using methyl orange as an indicator. Heat the solution to boiling and, while stirring, add 10 ml of $BaCl_2$ solution drop by drop. Continue boiling the solution for 15 min and allow to simmer for 2 h just below boiling. Filter through an ashless filter paper and wash the precipitate repeatedly with hot water until silver nitrate ($AgNO_3$) solution shows no precipitate with 1 drop of the filtrate. Place the wet filter paper containing the precipitate of barium sulfate ($BaSO_4$) in a weighed platinum, porcelain, silica or refractory

crucible, allowing a free access of air by folding the paper over the precipitate loosely to prevent spattering. Smoke the paper off gradually and at no time allow it to burn with a flame. After the paper is almost consumed, raise the temperature to approximately 925°C and heat to constant weight. The value so obtained and corrected for the blank determination (see d below) represents the sulfate sulfur of the coal.

d. Make a blank determination following the same procedure and using the same amounts of all reagents as described in Steps (a), (b), and (c) above.

2. Pyritic Sulfur

a. Transfer the sample obtained from the HCl extraction of sulfate sulfur to a 250-ml Erlenmeyer flask and add 50 ml of HNO_3 (1 + 7). Fit a cold-finger condenser into the neck of the flask, and either boil for 30 min or let it stand overnight at room temperature. Rinse the cold-finger condensor with HNO_3 (1 + 7), filter the contents of the flask through a medium-texture, double acid-washed filter paper, and wash six times with HNO_3 (1 + 7), collecting the filtrate and washings in a 600-ml beaker. Discard the residual coal on the filter paper and retain the filtrate for determination of iron, which is a measure of pyritic sulfur in coal.

Alternative method for determination of iron by Atomic Absorption Spectroscopy - Dilute the filtrate obtained in (a) above to 200 ml with water. Transfer a 50-ml aliquot of this solution to a 200-ml volumetric flask and add 10 ml of lanthanum solution (weight of sample may be varied to eliminate aliquot). Dilute to volume with water. Prepare a standard by combining 10 ml of 1000 ppm iron solution and 10 ml of lanthanum solution in a 100 ml volumetric flask and diluting to volume with water. Prepare a blank solution by combining 30 ml of HNO_3 (1 + 7) and 10 ml of lanthanum solution in a 100 ml volumetric flask and diluting to volume with water. Determine absorbences of the blank solution, standard and the sample at 372 nm using an air-acetylene flame.

NOTE 1: The wavelength of 372 nm is chosen for the determination to provide a less sensitive line and wider linear range for the iron absorbence. Linearity exists with concentration in this range for iron absorbence. Linearity in this range of iron concentration should be checked for each individual instrumental step and appropriate dilutions made if necessary. Alternatively, the 248.3 nm line may be used.

NOTE 2: If concentration mode is used and the unknown is bracketed, a blank is unnecessary.

3. Calculation

 a. Sulfate sulfur.. Calculate the percentage of sulfate sulfur in coal as follows:

$$\% \text{ Sulfate Sulfur} = [(A-B) \times 13.735]/W$$

where,

    A = g of $BaSO_4$ precipitate.
    B = g of $BaSO_4$ in the blank.
    W = g of sample.

 b. Calculate the percentage of pyritic sulfur, when the iron determination is made by atomic absorption, as follows:

$$\% \text{ Pyritic Sulfur } \frac{C-A}{B-A} = \frac{4.58}{W}$$

where,

    A = absorbence of blank.
    B = absorbence of standard.
    C = absorbence of sample.
    W = weight of sample extracted as selected for sulfate or pyritic determination.

 If values higher than 5% pyritic sulfur are obtained, a new sample solution should be prepared from 20 ml of the filtrate (Section 2. (a)) and 10 ml of lanthanum solution, diluted to 100 ml and the value obtained with this solution x 2.5 = percent pyritic sulfur.

 c. Organic Sulfur. The percentage of organic sulfur is obtained by subtracting the sum of the percentages of sulfate and pyritic sulfur from the percentage of total sulfur as determined by the Eschka Method.

4. Precision

 a. Repeatability. Results of consecutive determinations carried out on the same sample in the same laboratory by the same operator using the same apparatus should not differ by more than the following:

    (1) Sulfate Sulfur   0.02
    (2) Pyritic Sulfur (under 2%)   0.05
    (3) Pyritic Sulfur (over 2%)   0.10

 b. Reproducibility. The means of results of duplicate determinations carried out by different laboratories on representative samples taken from the same bulk sample should not differ by more than the following:

    (1) Sulfate Sulfur   0.04
    (2) Pyritic Sulfur (under 2%)   0.30
    (3) Pyritic Sulfur (over 2%)   0.40

. ALTERNATIVE METHOD FOR THE DETERMINATION OF FORMS OF SULFUR IN COAL

ι alternative method for the determination of forms of sulfur in coal can be
ımmarized as follows: the pyritic sulfur content in the coal is determined
' the oxidation of pyrite to ferric sulfate and subsequent estimation gravi-
ιtrically as barium sulfate, rather than by atomic absorption estimation of
·on as described in the ASTM method.

A.   REAGENTS

   1.   Bromine Water. Reagent grade bromine is added to distilled
        water until a saturated solution is obtained. The bromine
        saturated water is decanted off to·make reagent (see 2 below)

   2.   Bromine/HCl Solution. Add 250 ml of concentrated HCl to
        250 ml of water and add 500 ml of saturated bromine water,
        mixing well.

   3.   Barium Chloride Solution: 10% (W/V) in water.

   4.   HCl Solution for Sulfate Sulfur Determination: HCl/H_2O (2/3
        by volume).

   5. HNO_3 Solution for Pyritic Sulfur Determination:
        HNO_3/H_2O (1/7 by volume).

B.   PROCEDURE

   1.   1 g of coal is weighed into a 250-ml beaker, 50 ml of HCl
        (2/3) are added, and the sample is refluxed for 1/2 - 3/4 h.

   2.   The solution is cooled, filtered through 11 cm No. 40 Whatman
        filter paper and washed with hot distilled water. The fil-
        trate and washings are collected in a 400-ml beaker while the
        filter paper and residue are placed in the original beaker.

   3.   The filtrate from (2) above is adjusted to a methyl orange
        end-point (pH 3-4) if necessary, and heated to boiling.
        $BaCl_2$ solution is slowly added with stirring. The solution
        is allowed to sit for 1 h at this temperature and then kept
        overnight at room temperature. The $BaSO_4$ precipitate is
        collected over 11 cm No. 42 Whatman filter paper and washed
        with ·hot distilled water until free of the chloride ion. The
        filter paper is then ignited off and the $BaSO_4$ is ignited at
        about 925°C for 1/2 h, cooled and weighed.

$$\% \text{ Sulfate Sulfur} = \frac{\text{wt of } BaSO_4 \times 13.74}{\text{wt of sample}}$$

79

4. The filter paper and residue from (2) above is placed in the original 250-ml beaker and macerated with a glass rod; 50 ml of HNO$_3$ are then added and the contents are refluxed for 1/2 - 3/4 h.

5. The solution is filtered through 15 cm No. 40 Whatman filter paper and washed with hot distilled water. The filtrate and washings are collected in a 400-ml beaker, adjusted to methyl orange end-point if necessary, and 10 ml of bromine water/HCl solution are added. The solution is boiled until clear and BaCl$_2$ solution is added. The rest of the procedure is the same as described in (3) above.

$$\% \text{ Pyritic Sulfur} = \frac{\text{wt of BaSO}_4 \times 13.74}{\text{wt of sample}}$$

NOTE: The BaSO$_4$ precipitate is washed with hot dilute HCl (1/25) if an appreciable discoloration due to iron is noted.

III. DETERMINATION OF TOTAL SULFUR BY ESCHKA METHOD (ASTM D3177-73)

A. SUMMARY OF THE METHOD

The Eschka method involves mixing a coal sample with a mixture of MgO and Na$_2$CO$_3$ (called the Eschka mixture) and igniting the mixture in a bomb calorimeter under 30 atm of oxygen. The SO$_2$ produced by combustion is absorbed by the Eschka mixture and is converted to the sulfate form. The residue in the bomb is leached with hot water, and the sulfate is precipitated as BaSO$_4$. After the BaSO$_4$ is filtered and dried, it is weighed to give the total sulfur in coal.

B. PROCEDURE

The basic procedure involves mixing intimately about 1 g of coal with 3 g of Eschka mixture (2 g calcined MgO + 1 g anhydrous Na$_2$CO$_3$). Approximately 1 g of this mixture is placed in a bomb calorimeter and filled to 30 atm with oxygen. The bomb is placed in a water bath, the mixture is ignited, and the bomb is allowed to cool for at least 10 min. The pressure is then slowly released, and the bomb and the residue are thoroughly washed with hot water. The residue is digested with hot water for about 1 h after which it is filtered and the insoluble residue is washed at least 5 times with hot water. The filtrate is made slightly acidic with dilute HCl, heated to boiling and excess BaCl$_2$ solution is added drop by drop while stirring. The heating is continued for another hour,

after which the precipitate is filtered, washed with hot water
until the washings are free of the chloride ion, dried and weighed.
The amount of total sulfur in the sample is estimated as follows:

$$\% \text{ Total Sulfur:} \quad \frac{\text{wt of BaSO}_4 \text{ Precipitate} \times 13.75}{\text{wt of sample}}$$

APPENDIX C

MODIFIED LECO METHOD FOR TOTAL SULFUR AND CHLORINE DETERMINATION IN COAL

MODIFIED LECO METHOD FOR TOTAL SULFUR AND CHLORINE DETERMINATION IN COAL

I. SUMMARY OF THE METHOD

A coal sample is burned at 1300 to 1350°C in a flowing medium of oxygen. The sulfur dioxide, sulfur trioxide, and chlorine formed are absorbed in a hydrogen peroxide solution producing sulfuric and hydrochloric acids. The total acid content is determined by titration with standard sodium hydroxide solution. The titrated solution is further treated with mercuric oxycyanide solution to provide correction to the total acid determined as above for the hydrochloric acid content.

A. REAGENTS

(1) 0.05 N standard sodium hydroxide solution.

(2) 0.01 N standard sulfuric acid solution or prepared by diluting 0.1 N standard solution.

(3) Mercuric Oxycyanide Solution. Dissolve 0.25 g of mercuric oxycyanide powder in 20 ml of distilled water. Prepare one portion per sample boat and four portions for blanks for each set of samples. Discard this solution into the titration waste container if it is not used in 2 or 3 days.

NOTE: Mercuric oxycyanide is highly poisonous and will explode when touched by flame or by percussion.

(4) Hydrogen Peroxide Solution (1%). Dilute 100 ml of 30% H_2O_2 solution with distilled water to 3 l. Discard this solution if not used for 2 or 3 days.

(5) Methyl Purple Indicator Solution.

B. APPARATUS

Use LECO Model No. 534-500 total sulfur analyzer equipped with Model No. 571-500 (2-tube, 1.5 kW) resistance furnace and Model No. 517200 (manually operated) acid-base titration unit.

II. PROCEDURE

A. START-UP

1. Preheat resistance furnace to a temperature of 1350°C.

2. Prepare hydrogen peroxide and mercuric oxycyanide solutions.

3. Place the oxygen baffle in the combustion tube, fill the titration vessel with hydrogen peroxide solution, and adjust the oxygen flow to 1 1/min.

4. Fill pre-cleaned back titration buretts with fresh sulfuric acid and sodium hydroxide solutions.

5. Make sure that there is sufficient capacity in the titration waste container to receive the day's waste.

B. SAMPLE ANALYSIS SEQUENCE

1. Weigh about 0.2 g of the coal sample to the nearest 0.1 mg and spread it in a clay combustion boat.

2. Fill the titration vessel half full with 1% hydrogen peroxide solution. Add 10 drops of methyl purple indicator solution and adjust the pH with dilute sulfuric acid (0.01 N) until the green colour just turns gray or reaches the green-gray transition.

3. Put the boat containing the coal sample in the combustion tube so that the center of the boat is four inches from the center of the hot zone and replace the oxygen baffle.

4. After 1-1/2 min push the boat into the center of the hot zone, removing the oxygen baffle only as long as necessary to perform the operation quickly.

5. After 7 min of combustion (5-1/2 min with the boat in the hot zone), titrate with 0.05 N sodium hydroxide solution until the purple colour fades, just short of the end-point.

6. After 8 min of combustion (6-1/2 min with the boat in the hot zone) disconnect the rubber hose from the ceramic combustion tube outlet and rinse the rubber hose and bubbler three times with distilled water into the titration vessel.

7. Reconnect the rubber hose to the combustion tube and complete the titration with sodium hydroxide solution.

8. Add 20 ml of mercuric oxycyanide solution to the contents of the titration vessel.

9. Titrate the liberated hydroxyl ion with dilute (0.01 N) sulfuric acid solution.

10. Drain and rinse the titration vessel and remove the boat from the combustion tube.

C. SHUTDOWN

1. For each set of samples, run a dilute sulfuric acid (0.01 N) blank in triplicate on the mercuric oxycyanide solution.

2. Reduce the furnace temperature to 816°C.

   NOTE: For optimum performance of the furnace heating elements the temperature should not go down below 816°C even during periods it is not being used.

D. CALCULATION

S = wt% sulfur in coal (as determined basis).

A = units of 0.05 N sodium hydroxide used (LECO burette "%" units).

B = ml of 0.01 N sulfuric acid used in full determination.

C = ml of 0.01 N sulfuric acid used in blank determination for the mercuric oxycyanide solution.

W = weight of sample in grams.

Cl = wt% of chlorine in coal (as determined basis).

R = 1.133, if no standards are run with the sample set; otherwise:

$$\frac{\text{known sulfur content of the standard coal}}{\text{average sulfur content by titration of three standard samples}}$$

$$S = R \times \frac{0.5}{W} A - \frac{(B-C)}{31.28}$$

$$Cl = \frac{B-C}{W} \times 0.0355$$

APPENDIX D

SURFACE AREA AND PORE VOLUME DETERMINATION
BY LOW TEMPERATURE NITROGEN ADSORPTION

SURFACE AREA AND PORE VOLUME DETERMINATION
BY LOW TEMPERATURE NITROGEN ADSORPTION

. ## SUMMARY OF THE METHOD

Surface area of a solid is determined by physical adsorption of an adsorbate at its boiling point. In general, by nitrogen adsorption at liquid nitrogen temperatures, the quantity of gas required to form a complete monolayer of gas molecules is measured. The surface area of the solid is then calculated using the cross-sectional area of the gas molecule. Outgassing of the sample before measuring the amount of gas adsorbed is essential to ensure reproducible results. While many theories on gas-adsorption have been proposed, adsorption measurements are generally interpreted using the BET Theory (Brunauer, Emmett and Teller) for multilayer adsorption.

I. ## BET DETERMINATION

Three factors must be known in order to determine the specific surface area (area per gram) of a powder sample:

(1) Weight of the sample.

(2) Relative pressure.

(3) Weight of adsorbate adsorbed on the sample surface as a function of relative pressure in the range $0.05 < P/P_0 < 0.35$.

The assumptions, restrictions and applications of BET multilayer theory are discussed in all modern texts on surface chemistry. The reversible adsorption of an adsorbate is given by the BET equation as:

$$\frac{1}{x\left[\frac{P_0}{(P-1)}\right]} = \frac{C-1}{x_m\ C}\ \frac{P}{P_0} + \frac{1}{x_m\ C}$$

where,

x = weight of adsorbate adsorbed at relative pressure P/P_0.

P = partial pressure of adsorbate.

P_0 = saturated vapour pressure of adsorbate.

x_m = weight of adsorbate required to completely cover one monolayer.

C = a constant that is a function of the heat of condensation and adsorption of the adsorbate.

The BET equation yields a straight line when $\dfrac{1}{x\left[\dfrac{P_0}{(P-1)}\right]}$ is plotted

versus P/P_0. The value of x_m, the weight adsorbed for a mono-layer can be calculated from the slope and intercept of the BET plot as follows:

$$S = \text{Slope:} \quad \frac{C-1}{x_m\,C}$$

$$I = \text{Intercept:} \quad \frac{1}{x_m\,C}$$

Solving for x_m yields:

$$x_m = \frac{1}{S+I}$$

NOTE: The BET plot is usually found to be linear in the range P/P_0 = 0.05-0.35. Thus, data outside this range should be avoided.

The total surface area of the sample, S_t, is calculated using the following equation:

$$S_t = \frac{x_m\ N\ A_{cs}}{M_a}$$

where,

x_m = weight of adsorbate required for one monolayer.

N = Avagadro's Number (6.023×10^{23}).

A_{cs} = Cross-sectional area of the adsorbate molecule (as given in the Table 13).

M_a = Molecular weight of the adsorbate.

The specific surface area of the sample is given by:

$$S = S_t/\text{weight of sample}$$

92

Table 13. Effective Molecular Areas of Various Adsorbates

Adsorbate	Area, $m^2 \times 10^{20}$
Nitrogen[a]	16.2
Krypton	19.5
Argon	14.2
Xenon	25.0
Oxygen	14.0
Ethane	20.5
Butane	46.9

[a]Nitrogen is usually the preferred adsorbate since the cross-sectional area has been exactly determined by several investigators.

I. SINGLE POINT BET METHOD

SUMMARY OF THE METHOD

This simplified method as an alternative to the multipoint BET Method is based on the fact that the intercept in a BET plot with nitrogen as the adsorbate is generally small when compared to the slope and hence can be ignored. If the intercept is assumed to be zero, the value of x_m tends to be excessively large. However, this is somewhat compensated as the measured value of the slope tends to increase if the intercept is assumed to be zero.

By assuming the intercept to be zero, the BET equation is simplified as:

$$\frac{1}{x \ (P_0/P-1)} = \frac{1}{x_m} P/P_0$$

or

$$x_m = x \ (1-P/P_0)$$

Thus, by measuring the amount of adsorbate adsorbed at a single value of P/P_0 (preferably P/P_0 = 0.3), the monolayer volume x_m can be calculated.

Substituting the value of x_m, the specific surface area (m^2/g) of the sample with N_2 as the adsorbate is calculated as:

$$S = \frac{3.98 \times x_m}{wt\ of\ sample}$$

IV. PORE VOLUME AND PORE RADIUS

SUMMARY OF THE METHOD

Vapours in equilibrium with a liquid contained in fine capillaries or pores will have depressed vapour pressures. In fact, if the pore is sufficiently small in diameter, the vapours will condense at pressures far below the normal. According to Kelvin equation, nitrogen gas will condense into all pores with radii less than 1500 Å at a relative pressure of 0.99. Thus, by measuring the volume of nitrogen adsorbed at a relative pressure of 0.99 and knowing the surface area, the average pore volume and the mean pore diameter can be calculated.

PROCEDURE

After thoroughly degassing a sample, adsorb a concentration of adsorbate corresponding to $P/P_0 = 0.99$ (Any value in the range 0.96 to 0.99 will be suitable). When adsorption is complete as indicated by a return to baseline on the recorder, remove the liquid nitrogen bath and desorb the adsorbate. Calibrate the signal with pure adsorbate. Convert the volume of nitrogen adsorbed to the volume of liquid nitrogen held in the pores using the equation:

$$V_{liq} = \frac{P_a\ V_{ads}}{RT}\ V_m$$

where,

P_a = ambient pressure.

V_{ads} = volume adsorbed per gram of adsorbent.

T = ambient temperature.

V_m = molar volume of liquid adsorbate (34.7 cm^3 for N_2).

Assuming that all the pores are uniform and cylindrical, the mean pore diameter is given by:

$$d\ (\mathring{A}) = \frac{4\ V_{liq}}{S} \times 10^4$$

where V_{liq} is the volume of all pores in the sample with a specific surface area S.

C-2